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Thermally Activated Bentonite As a Supplementary Cementitious Material – A Review

Amer A. Al-Hammood [a*], **Qais J. Frayyeh** [b], **Waleed A. Abbas** [c]

a Civil Engineering Dept., University of Technology, Baghdad, Iraq, 42402@student.uotechnology.edu.iq

b Civil Engineering Dept., University of Technology, Baghdad, Iraq, 40012@uotechnology.edu.iq

c Civil Engineering Dept., University of Technology, Baghdad, Iraq, 40017@uotechnology.edu.iq

*Corresponding author.

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ABSTRACT

Bentonite is a mixture of clay and non-clay minerals. Montmorillonite clay mineral is a dominant mineral in bentonite. Silica and alumina bond in the crystal structure of montmorillonite. Therefore, they cannot contribute to the pozzolanic reaction. Heat treatment of bentonite leads to the destruction of the crystal structure of montmorillonite and converting silica and alumina to reactive phases. Thermally activated bentonite (TAB) is a relatively low reactive pozzolan when used as partial replacement of Portland cement modifies both fresh and hardened properties of cement paste, mortar, and concrete. The most desired effects of TAB are: improve segregation resistance, reduce the rate of strength gain, and enhance concrete durability against sulfates, chlorides, and acids, in addition to economic and ecological beneficiations. This paper provides information related to heat treatment of bentonite clays and montmorillonite minerals, and their effects on the paste, mortar, and concrete when used as a partial replacement of Portland cement.

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1. INTRODUCTION

The primary sources of supplementary cementitious materials (SCMs) are: naturally formed materials such as volcanic materials and diatomaceous earth, and by-products or wastes from some industries such as fly ash, silica fume, and blast furnace slag. Unfortunately, these sources are available in limited areas. Moreover, the increasing demand for SCMs necessitates investigation for additional sources. The clays and shale represent the successful additional sources due to their widespread and their richness in the oxides of silicon, aluminum, and iron. These oxides are often present combined in the crystal structure of clay minerals.Therefore, they exhibit low chemical reactivity. Heat treatment of clay leads to the destruction of the crystal structure of clay minerals, hence producing reactive phases of silica, alumina, and iron oxide. Clay minerals differ in chemical and mineral composition, which results in their different response to thermal activation [1]. Bentonite is impure clay consisting mainly from montmorillonite mineral [2]. The utilization of thermally activated bentonite (TAB) in concrete production is still uncommon, despite the thermally activated montmorillonite (TAM) has been successfully used in important projects such as Flaming Gorge Dam (completion in 1963) on the Green River in the USA [3].

2. THERMAL ACTIVATION OF BENTONITE

Heating leads to subsequent transformations in the structures of minerals that form bentonite. Montmorillonite mineral is the dominant mineral in bentonite. Therefore, the structural transformations in montmorillonite mineral representthe bentonite changes due to heating. Montmorillonite and bentonite pass into four successive stages during heating [4, 5]:

1. Dehydration stage: loss of uncombined water (adsorbed and interlayered). The temperatures requirecompleting this stage varies according to initial moisture content, size of clay particles, type of cations fill the interlayer spaces and the presence of defects in mineral structure [6]. The temperatures recorded for dehydration completion were: 100 – 150 °C [5], 150°C [7], 160°C for sodium montmorillonite and 180°C for calcium montmorillonite [8], and 200°C [1, 9].
2. Dehydroxylation stage: loss of hydroxyl group from the mineral structure. The most of OH group binds in aluminum octahedral coordinate ($Al^{[VI]}$) sheet. Therefore, the dehydroxylation leads to convert $Al^{[VI]}$ to 5-fold coordinate ($Al^{[V]}$) and tetrahedral coordinate ($Al^{[IV]}$) [1, 4]. The structural transformation in octahedral sheet leads to loss the crystallinity of 1:1 clay minerals like kaolinite, but the 2:1 clay minerals like montmorillonite conserve their crystallinity despite the transformations in octahedral sheet [1]. The temperatures reported for the initiation and completion of the dehydroxylation ranged from 400 to 800 °C [1, 2, 4-8, 10].The factors that influenced the dehydroxylation temperature are: the type of exchangeable ions and chemical composition of mineral [5, 6] especially the presence of iron in the mineral structure [6].
3. Amorphization stage: partially or completely decomposition of crystalline structure and formation of new amorphous and/or cryptocrystalline reactive phases. This stage represents the goal of the thermal activation process; the optimum temperature required to achieving this aim was determined precisely in each experiment but there is no specific degree. According to Aljubury [2], the structure of Iraqi calcium bentonite is completely collapsed at 700°C while higher degrees were reported: 800°C [4, 7], 830°C [8, 10], and 900°C [5, 6]. It is not certain what causes the differences in temperatures required for amorphization, but the differences may be attributed to the calcination program e.g: heating rate, holding period, and cooling rate. The types of montmorillonite and impurities have little effect on amorphization temperature [10].
4. Recrystallization stage: formation of new crystalline inert phases due to high temperature effect; recrystallization was noticed at 920°C [7, 10], 1050°C [6], and (1000 – 1100) °C [4].

Thermal activation program followed in each study illustrate in Table 1.

3. POZZOLANICITY OF TAM AND TAB

The pozzolanic reactivity of TAM and TAB were investigated either with lime or with Portland cement. The proofs of the pozzolanic reaction include the decline of reactants and the formation of reaction products.

Taher [11] studied the chemical reaction between TAM and lime; the mix of 80% TAM at 1000°C and 20% lime, cured under 10-atmosphere pressure for 24 hours, was developing compressive strength of 55MPa. The reaction products detected by scanning electron microscope (SEM) were mainly C-S-H and C-S-A-H. In addition to the formation of C-S-H, the formation of C_4AH_x was also observed due to lime and TAM reaction [8, 10].

The reactivity of TAM with lime depends on activation temperature. Moreover, the structure of produced C-S-(A)-H was strongly affected by the activation temperature, the incorporation of Al in the structure of C-S-H proportions to the reactivity degree [4]. Figure 1 illustrates the effect of activation temperature on the percentage of reacted montmorillonite, and Al/Si in the produced C-S-(A)-H.

TABLE 1: Bentonite and montmorillonite activation programs proposed by several researchers.

	Activation temperature (°C) / Activation period (min.)						
Taher [11]	550/240	700/240	800/240	900/240	1000/240		
Trümer et al. [9]	900						
He et al. [10]	700	800	900				
He et al. [8]	730	830	930				
Penson [3]	800/240	850/240	900/240	1000/240			
Aljubury [2]	200/120	300/120	400/120	550/120	700/120		
Darweesh [12]	800						
Mirza et al. [15]	150/180	250/180	500/180	750/180	950/180		
Garg and Skibsted [4]	110/120 750/120	200/120 800/120	300/120 850/120	400/120 900/120	500/120 1000/120	600/120 1100/120	700/120
Fernandez et al [1]	600/60	800/60					
Memon et al. [16]	200/1440						
Ahmad et al. [13]	500/180	900/180					
Rehman et al. [14]	100/180 800/180	200/180 900/180	300/180 1000/180	400/180	500/180	600/180	700/180
Laidani et al. [18]	800/180	800/240					
Laidani et al. [7]	600/120 800/180	600/180 800/240	600/240 900/120	700/120 900/180	700/180 900/240	700/240	800/120

The pozzolanic reaction was also observed with Portland cement; the replacement of Portland cement by TAB at different percentages leads to gradual consumption of $Ca(OH)_2$ as shown in Figure 2 [12]. Fernandez *et al.* [1] stated that TAM, at 600°C, seems to be effective in depleting $Ca(OH)_2$ at 30% substitution of Portland cement in both cement paste and mortar. Grag and Skibsted [9] reported 36.8% consumption of TAM due to pozzolanic reaction in the paste consists of 30% TAM at 800°C and 70% white cement, using 0.5 water to powder ratio at 365 days age.

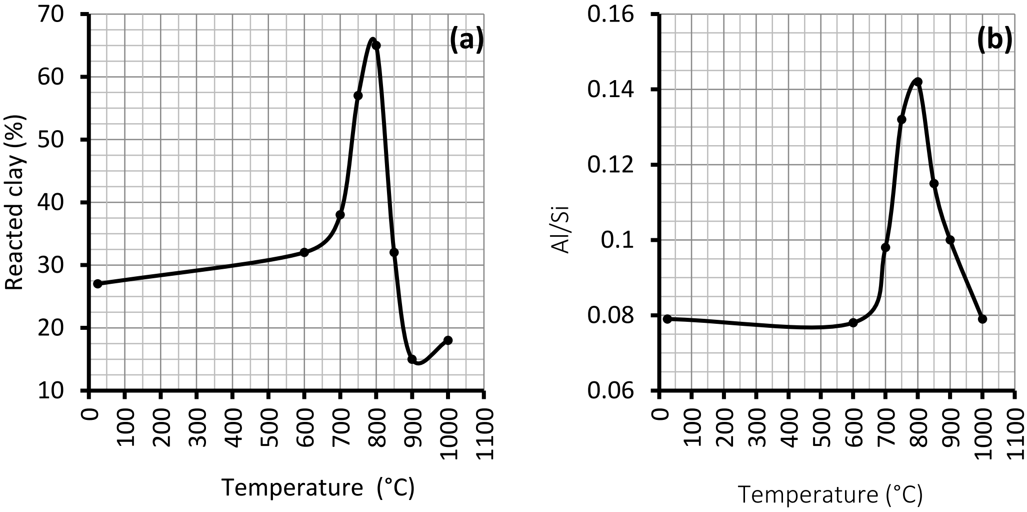

Figure 1: (a) Reacted montmorillonite with lime at different activation temperature and (b) Al incorporation in C-S-(A)-H represented by Al/Si ratio due to activation temperature [4].

4. EFFECTS OF CEMENT REPLACEMENT BY TAB IN CEMENT PASTE

4.1.Fresh properties of cement paste

Darweesh and Nagieb [12] studied cement substitution by TAB at (3, 6, 9, 12, and 15%) in cement paste; the study concluded that TAB incorporation causes linearly increase in water demand to achieve standard consistency of the paste, the stiffening effect was attributed to fineness, absorption, and pozzolanicity of TAB. The same results were reported at high replacement levels (30, 50, and 70%)[3]; but Trümer *et al.* [9] mentioned that TAB at 900°C and 30% substitution reduceswater demand slightly.The conflicting results indicate the importance of chemical and mineral composition, and thermal activation program in the behavior of TAB. On the other hand, the retardation effect on both initial [9, 12] and final setting time was observed [3, 9, 12]; the extension in setting time proportioned to TAB content [12]. Both higher water demand [3, 12] and lower reactivity of TAB [3, 9, 12] cause the retardation effect. Significant accelerated effect of initial setting time was noticed at 70% substitution due to apparent quicker absorption of TAB [3].

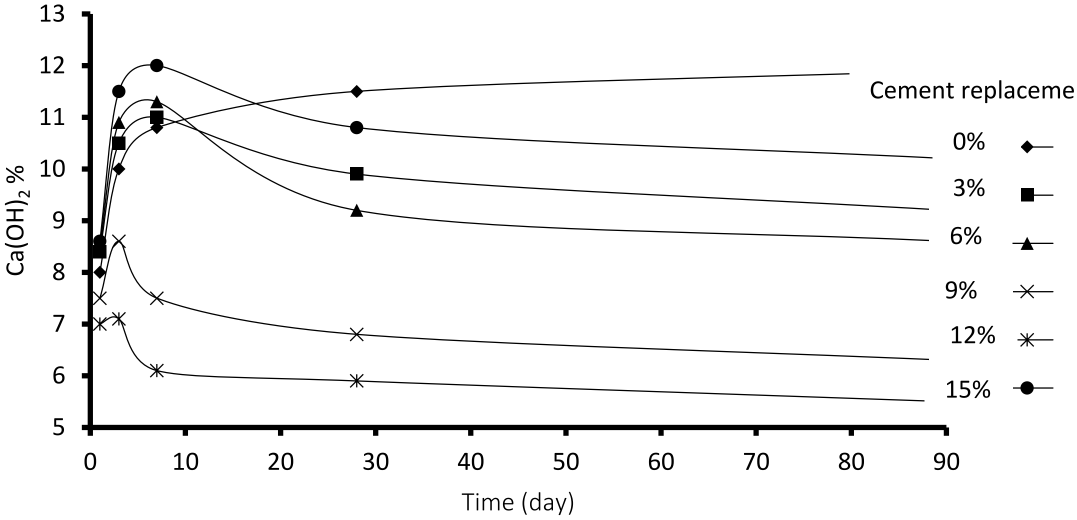

Figure 2: Gradual decrease in $Ca(OH)_2$ content due to cement replacement by TAB at different levels [12].

4.2. Hardened properties of cement paste

Cement paste with standard consistency shows increases in compressive strength and bulk density, and decreases in porosity due to cement substitution by TAB at 12% or less. This is attributed to densifying microstructure by pozzolanic reaction and filling effect of bentonite particles. The reverse effect was observed at 15% replacement due to higher water demand [12].

5. EFFECTS OF CEMENT REPLACEMENT BY TAB IN CEMENT MORTAR

5.1. Fresh properties of cement mortar

Laidani *et al.* [7] studied the fresh properties of self-compacted mortars containing Ca-bentonite activated at 800°C for 3 hours and Na-bentonite activated at 800°C for 4 hours. The replacement percentages were (5, 10, 15, 20, 25, and 30%) for each type of TAB. The results obtained from the mini-slump flow test and V-funnel flow test are illustrated in Figure3. It is obvious that the bentonite type plays an important role in the flow behavior of mortar. In general, the incorporation of TAB into self-compacted mortar leads to increase in the dosage of superplasticizer admixture to maintain flow characteristics.

5.2. Hardened properties of cement mortar

TAM characterized by its low reactivity in the comparison with activated kaolinite [1].Therefore, the cement replacement by TAM or TAB leads to reduction of the rate of strength gain, but there is wide dissimilarity in the results of compressive strength of mortars that contain TAM or TAB. This is attributed to differences in chemical and mineral composition of both montmorillonite and bentonite types in addition to activation program and replacement level.

At 20% cement replacement, the strength activity indexes at 7 and 28 days were reported at different activation temperatures: 70 and 85% respectively at 500°C [13], 93 and 94% respectively at 800°C [14], and 101 and 104% respectively at 150°C [15].

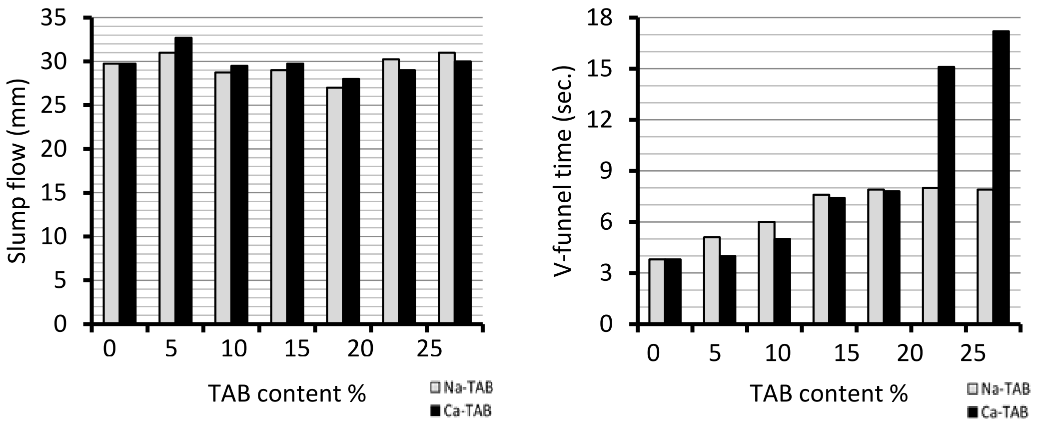

Figure 3: Flow properties of mortars containing Ca- TAB and Na-TAB [7].

At early ages of mortars (28 days or less), and replacement levels more than 20%, significant reductions in compressive strength were reported and the reduction increases as the replacement increases [3, 9, 14,15]; but the reduction in compressive strength disappears at later ages (56 – 90 days) or is reversed into an increase at 30% replacement [3, 9].

At relatively low replacement levels (3 – 15%), no reductions in compressive strength were reported at all ages [7, 14, 16].Moreover, significant increases in compressive strength were reported at (3–10% replacement at 28 days [14, 16]. `

Blend TAB with metakaolin 1:1 leads to increase compressive strength at 90 days by 10% more than the compressive strength of control mortar [17].

Bond strength with brick masonry of mortar containing 25% TAB at 150°C is similar to that of reference mortar [15].

TAB at 900°C and 30% replacement modifiesthe microstructure of mortar by reduction of overall porosity and refinement of the pore structure by increase of pore fraction less than 10 nm, as shown in Figure 4 [9].

Because of pozzolanic reaction and pores refinement, TAB improves the durability of cement mortar against alkali-silica reaction at 30% replacement [9] and sulfates attack at 20% replacement [14]. The depth of carbonation of mortar contains 30% TAB is twice the carbonation depth of reference mortar [9].

At elevated temperature (600-1000°C), the performance of mortars contain TAB, represented by mass loss and residual strength is slightly better than control mortar [7].

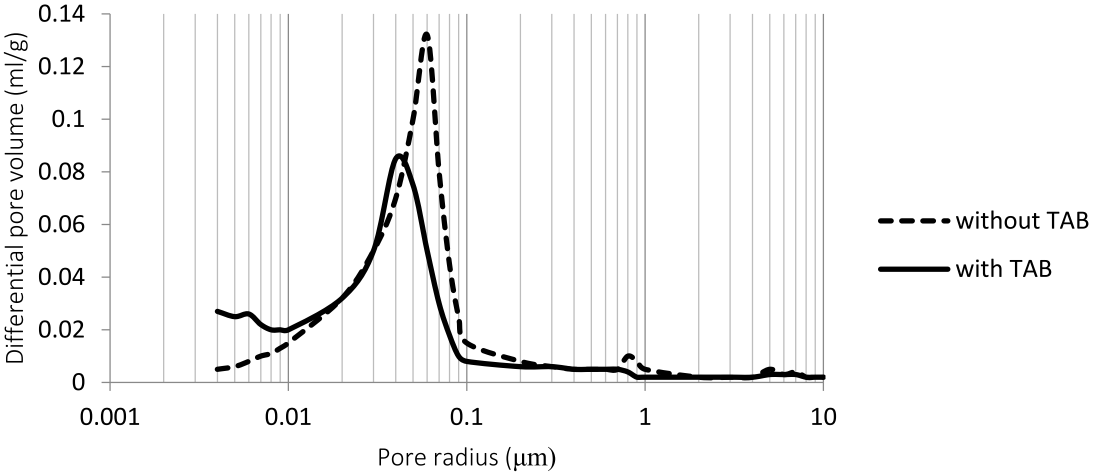

Figure 4: Pore size distributions of 91days old mortars with and without 30% TAB [9].

6. EFFECTS OF CEMENT REPLACEMENT BY TAB IN CONCRETE

6.1. Fresh properties of concrete

Portland cement replacement by TAB at (3 – 21%) leads to reduction of the slump value of concrete; the reduction in slump is proportionally linearly with TAB content, for instance, 50mm slump for control concrete reduces to 35mm for concrete at 21% replacement [16]. Fresh density of concrete decrease as TAB content increase, for example, fresh density of 2482 kg/m^3 for control concrete decreases to 2275 kg/m^3 at 21% replacement [16].

Fresh properties of self-compacted concrete containing TAB were investigated by Laidani *et al.* [18]; the study concluded the following results:

- The increase in the percentage of replaced cement by TAB decreases the flowability of concrete, which requires an increase in superplasticizer dosage to achieve the targeted slump.
- TAB incorporation leads to an increase in concrete viscosity.
- TAB increases the passing ability of concrete.
- Decreases the tendency to segregation as TAB content increase.

6.2. Hardened properties of concrete

Portland cement replacement by TAB decreases the rate of strength gain due to low reactivity of TAB.Therefore, the reductions in compressive strength of concrete were recorded at early ages (1 – 21) days at any level of substitution (3 – 50%) [9, 13, 15, 16, 18] except slight increments reported by Laidani *et al.* [18] at 10 and 15% substitution in self-compacted concrete; the decrement levels vary according to bentonite type, activation degree, substitution level and concrete mix proportion. The higher reductions in strength were noticed at higher replacement levels (30 – 50%) [13, 15, 18], at lower activation temperature [9, 13, 15, 18], and at leaner mixes [13, 15, 18]. At 28 days age, the differences in strength tend to decrease especially at moderate levels of substitution (20 – 30%) [9, 15, 16, 18] while low substitution levels (3 – 15%) increase the strength [16, 18] and high replacement levels (30 – 50 %) decrease the strength [15, 18]. At later ages (56 – 90) days, the rich concrete mixes containing TAB at 800°C develop compressive strength more than control mixes at replacement levels (5 – 30 %) [18], while at lower activation temperature the low substitution (3 – 15%) increase the strength [16], and high substitution (20 – 50%) decrease the strength [13, 15].

At the same conditions, the reduction in modulus of rupture is about half the reduction of compressive strength. In reinforced concrete beam, at 25% replacement, a reduction of 30% in cracking load and reduction of 20% in ultimate flexural strength were reported; these reductions associated with an increase in fracture deflection by 70% which enhance the ductility of flexural members [15].

Water absorption decreases as TAB content increase, for example, 21% replacement leads to reduces absorption by about 30% [16].

TAB enhances concrete durability by:

- Increase the resistance to acids attack (sulfuric acid and hydrochloric acid) at (3 – 21%) replacement [16],
- significant reductions in chloride-ion penetration reach to 64% at 15% replacement [18]
- Reduction of chloride migration coefficients by 66% at 30% replacement [9].

On the other hand, TAB reduces the resistance of concrete to the frost action at 30% replacement [9].

7. BENEFITS OF TAB AS AN SCM

There are common benefits forutilization ofthe pozzolanic materials as a partial replacement for Portland cement in the production of concrete, and the foremost of these benefits are the sustainability aspects. Each pozzolanic material has intrinsic properties that distinguish it from other materials and makes it more suitable for specific uses in concrete. The most popularcalcined clay as a pozzolanic material is the metakaolin (MK). Therefore, it is useful to compare TAB to MK to highlight the potential specific uses of TAB.

MK characterized by its high pozzolanic reactivity which leads to increase both the total heat of hydration and its generation rate [19, 20], while TAM and TAB characterized by their lower pozzolanic reactivity [1, 21-23]. In the alkaline conditions, the Si solubility of MK is greater than the Si solubility of TAM by 4 times and the Al solubility of MK is greater than Al solubility of TAM by 12 times [23]. The low reactivity of TAB makes it more suitable than MK in hot weather concreting and mass concrete.

According to ACI 222R [24], the $Ca(OH)_2$ consumption by the pozzolanic reaction may increase the risk of reinforcement corrosion. MK at 20% substitution or more may lead to fully remove of $Ca(OH)_2$ [19, 20]. The ability of TAB to portlandite consumption is about 50% of MK ability [22]. Therefore, TAB is better than MK for conserving the passive layer of reinforcement.

8. CONCLUSIONS

From reviewed researches, the following conclusions can be drawn:

1. Bentonite is a family of clays contains multiple types differ in chemical and mineral composition.
2. Thermal activation of bentonite clays leads to obtaining pozzolanic material, but there is no specific activation program due to differences in bentonite types.
3. TAB characterized by low specific gravity and high finesse in comparison with Portland cement.
4. TAB has a lower pozzolanic reactivity compared to metakaolin.
5. Portland cement substitution by TAB increases the cohesive of fresh mixture that leads to reduce flowability and increase segregation resistance.
6. Pozzolanic reaction of TAB modifies the microstructure of cementitious binder by reducing $Ca(OH)_2$ content, increasing C-S-H and C_4AH_x content, inserting Al in C-S-H structure, and refinement of pores in the cement matrix.
7. TAB incorporation reduces the rate of compressive strength gain, and the reduction propagates as TAB content increase; for purpose of maintain or increase the compressive strength at later ages, the replacement level shall be at (5 – 15%).
8. At (20 – 30 %) substitution, the durability of concrete and mortar enhance due to noticeable promote in the resistance to deterioration by sulfates, acids, chlorides, and reactive silica in aggregates.
9. TAB has negative effects on concrete resistance to carbonation and frost action.
10. Slight improvement in fire resistance of concrete and slight increase in ductile behavior of reinforced concrete beams were reported due to TAB incorporation.

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