Raw bentonite as supplementary cementitious material – a review

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Abstract. Bentonite is a type of clay that consists mainly of the montmorillonite mineral when it is finely ground and used as a partial replacement of Portland cement. The result is the low-cost and eco-friendly cementitious binder. Using this binder leads to modify both fresh and hardened properties of cement paste, mortar, and concrete. The desired modifications include; reduce the heat of hydration, reduce the absorption, promote both sulphates and acids resistance; the undesired effects include: increase water demand, reduce setting time, and declination of the mechanical properties. Although raw bentonite may meet the standard requirements for natural pozzolan, it's considering as a supplementary cementing material that still lacks conclusive evidence.

1. Introduction
Sustainable concrete is receiving increasing attention in research and applied fields. One of the strategies used in obtaining sustainable concrete is the use of supplementary cementitious materials (SCMs). Raw clays are attractive materials due to their low embodied energy. Because bentonite is widespread on a global scale [1], the investigation of its validity as an SCM has become the subject of many studies. This paper included a review of the researches done in the field of using raw bentonite as a partial substitution of cement.

2. Bentonite
The term bentonite is defined "any clay which is composed dominantly of a smectite clay mineral, and whose physical properties are dictated by this clay mineral" [1], the smectite content in bentonite may reach to 70% or more [1]. Smectite was formerly known as montmorillonite [2]. Montmorillonite consists of an octahedral sheet (O) sandwiching between two tetrahedral sheets (T) [2, 3], the structure of montmorillonite mineral illustrate in Figure 1.

In nature, bentonite is present as rocks consisting of a mixture of minerals. In addition to the predominant montmorillonite mineral, bentonite rocks contain clay minerals such as kaolinite, illite and palygorskite, and also contain non-clay minerals such as gypsum, quartz and calcite.

There are multiple species of smectite minerals: sodium montmorillonite, calcium montmorillonite, magnesium montmorillonite, ferrous montmorillonite, lithium montmorillonite and aluminum montmorillonite [2]. The type of bentonite is determined based on the dominant smectite in it, for example, calcium bentonite contains calcium montmorillonite as a major mineral, and sodium bentonite contains sodium montmorillonite as a major mineral, and so on. The general chemical formula of montmorillonite is: (Na,Ca)0.3(Al,Mg)2(Si4O10)(OH)2·nH2O [3,4]. The chemical
composition and physical properties of bentonite differ from one quarry to another and perhaps within the same quarry, and this difference is due to:
i. The type and quantity of the major montmorillonite.
ii. Types and quantities of minor minerals.

Figure 1: Montmorillonite structure [3].

Table 1 elucidates the differences in the proportions of the major oxides of the bentonite types used in previous researches.

|                | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | K₂O | Na₂O | SO₃ | Cl |
|----------------|------|-------|-------|-----|-----|-----|------|-----|----|
| Abali et al. [12] | 57.8 | 13.6  | 5.9   | 4.0 | 2.4 | 1.6 | ---  | 0.1 | ---|
| Ahmad et al. [6]   | 65.0 | 15.0  | 3.0   | 2.7 | 6.5 | 0.3 | 0.1  | --- | ---|
| Akbar et al. [20]  | 49.6 | 21.1  | 3.2   | 12.6| 3.6 | 2.1 | 0.4  | 0.2 | 1  |
| Aljubury [3]       | 41.6 | 13.2  | 3.9   | 9.9 | 4.1 | 0.4 | 1.2  | 0.2 | 1  |
| Karthikeyan et al. [16] | 49.6 | 21.1  | 3.2   | 0.7 | 3.6 | 2.1 | 0.4  | --- | ---|
| Mesboua et al. [10] | 56.4 | 17.4  | 1.8   | 1.4 | 2.8 | 1.7 | 3.2  | 0.1 | ---|
| Mirza et al. [5]   | 49.4 | 19.7  | 6.2   | 7.5 | 1.6 | 0.7 | 0.9  | --- | ---|
| Reddy et al. [9]   | 51.1 | 6.4   | 7.7   | 6.6 | 7.6 | 1.3 | 0.3  | --- | ---|
| Shabab et al. [15] | 52.1 | 13.4  | 7.5   | 12  | 2.5 | 2.6 | 0    | --- | ---|

* The values in the table are rounded to the nearest decimal.

Ground raw bentonite (RB), without any other treatments, was used as a partial substitution for Portland cement in many studies. Its use has modified some of the fresh and/or hardened properties of cement paste, mortar and concrete. This type of bentonite has been called "as is" bentonite [5] or "as received" bentonite [6].

RB characterized by its relatively low specific gravity and relatively high surface area with compared with Portland cement, therefore, the physical properties of the dry cementitious binder, consists of RB and cement, tend to modify as the RB content increases, for example, 30% cement replacement by RB decreases the specific gravity from 3.15 to 2.98 and increases the surface area from 2850 cm²/g to 5180 cm²/g [7].

3. Effects of cement replacement by RB in cement paste

3.1. Fresh properties of cement paste

The cement replacement by RB causes two opposite effects on the consistency of cement paste: the dispersing effect of fine bentonite particles which leads to increase paste fluidity [8], and the absorption effect which leads to increase the paste stiffening.
Sodium bentonite (Na-RB) has high water absorption, while calcium bentonite (Ca-RB) has a relatively low absorption [1]. The interaction between two effects appears at the low level of cement replacement by Ca-RB, if the absorption is dominant, the slight increases in water demand to obtain the standard consistency were reported at (5, 10 and 15)% replacement [9], while decreases in water demand at (5 and 10)% and no change in water demand at 15% were reported [7] due to dispersing effect of ultra-fine particles. At replacement levels, more than 15% of the absorption of Ca-RB is dominant and causes significant increases in water demand [7, 9].

The high absorption of Na-RB overcomes the dispersing effect of fine particles at any level of substitution, therefore, Mesboua et al. [10] noticed significant reductions in grout fluidity due to Na-RB substitution at all levels, the grout made of cementitious binder and water only, Figure 2 shows the effect of RB on mini-slump [11] value of grout.

![Figure 2: the relation between RB% and mini-slump value of grout [10].](image)

Fine bentonite particles provide additional nucleation sites that lead to promoting the hydration process and then accelerate setting time, and the bentonite absorption accelerates cement paste setting also; on the other hand, Portland cement replacement by RB reduces cement components C₃A and C₃S which response the paste setting then causes retardation the setting time. The interaction between RB effects leads to contradictory information about setting time; according to Targan et al. [7] the reduction in water demand associated with prolongation in initial setting time and vice versa, and the final setting time was accelerated in general; whereas Reddy et al. [9] reported retardation effect of RB on both initial and final setting time at all replacement levels.

The Na-RB incorporation in cement grout reduces bleeding and even eliminates it at 16% or more; besides, it causes reductions in fresh densities of grout proportion with RB content, for example, the density of reference grout was 1.63 g/cm³ and the density at 18% was 1.45 g/cm³ [10].

The partial substitution of Portland cement by RB leads to raising the volume expansion of the paste. The expansion's magnitude proportions with RB content, for example, 30% replacement increases expansion by 5mm in addition to the original expansion of reference paste [7]; moreover, further expansion was observed when RB used in conjunction with other SCMs e.g. fly ash, bottom ash and volcanic tuff [7, 12]. The increase in volume expansion may be attributed to the high swelling susceptibility of smectite [2].

3.2. Hardened properties of cement paste

Mesboua et al. [10] mentioned that Na-RB reduces both water absorption and compressive strength of hardened grout at 28 days, but the reductions values were differed, at 18% replacement the reduction in absorption was 24% from reference grout absorption while the reduction in compressive strength was only 6%; the decrease in absorption has been explained by three reasons: the formation of additional C–S–H due to pozzolanic reaction, filling micro pores by bentonite fine particles and reduction in water to binder ratio; but these explanations are supposed to lead to an increase in compression strength, or at least not to reduce it.
4. Effects of cement replacement by RB in cement mortar

4.1. Fresh properties of cement mortar
Kaci et al. [13] studied the effects of RB addition to cement mortar on its rheological behaviour in fresh state; the research included RB addition at low levels (0.1, 0.5 and 1) %, they reported escalations in rheopectic behaviour of mortar proportional to RB percentage that leads to reduce sagging mortar on vertical masonries; this advantage associated with disadvantage in pumpable mortar represented by flow blocking.

4.2. Hardened properties of cement mortar
The mortar specimens' tests were carried out to determine the strength activity index (SAI) which was used as a criterion in most standard specifications for determining the validity of material as an SCM. RB achieves the SAI requirements [5-7].

Mirza et al. [5] examined cement substitution by Ca-RB in mortar. The results show declines in compressive strength proportioned with Ca-RB content at all ages, Figure 3 shows the effects of the replacements of ordinary Portland cement (OPC) by RB on the compressive strength of mortar. This effect was confirmed by Ahmad et al. [6] and Targan et al. [7], on the other hand Selvaraj and Priyanka [14] mentioned that Na-RB cause strength reduction at (2.5, 5, 7.5, 10, 12.5, 17.5 and 20)% replacement while cause strength increment at 15% replacement, and Targan et al. [7] reported a slight increase in compressive strength for 5% substitution at ages (2, 7, 60 and 90) days and 10% substitution at (2 and 7) days. In general, the replacement of more than 15% causes reductions in compressive strength at all ages.

Figure 3: effect of OPC replacement by RB on the compressive strength of mortar [5].

Ahmad et al. [6] reported reductions in water absorption in mortars due to RB replacement and the optimum reductions at 30% substitution were 20% at 28 days and 33% at 56 days.

Incorporation of RB in mortar promote its resistance to sulphates attack represented by strength loss due to continues immersion in sulphates solutions, both 2% magnesium sulphate and 5% sodium sulphate cause less reduction in RB mortar strength compared with control mortar for 90 days immersion periods, the 30% replacement improves the best sulphates resistance [6].

5. Effects of cement replacement by RB in concrete

5.1. Fresh properties of concrete
The workability of concrete reduces due to RB incorporation; Figure 4 shows the effect of RB% on the slump of 1:2:4 concrete with 0.55 W/cm [6].

A slight reduction in peak temperature (5.4%) was observed in the centre of mass concrete at 25% replacement, and there is no change in the time required to temperature balance between surface and centre; on the other hand, the hybrid substitution (12.5% RB + 12.5% fly ash) leads to reduce peak temperature by 14.9% and shorten the balance time from 140 to 100 hours. The synergistic of fly ash and RB is more effective than RB or fly ash alone in reducing the maximum temperature and balance time [15].
5.2. Hardened properties of concrete

The compressive strength of concrete decreases due to cement replacement by RB, but there is no specific rule governing the relationship between RB content and the amount of strength loss. High levels of replacement (35-50)% lead to adverse reductions in compressive strength of about (45-60)% [6, 16]; moderate levels (15-30)% cause reductions of about (3-60)% proportioned to RB content [6, 9, 17, 18], but Karthikeyan et al. [16] reported increase compressive strength by 20% at 30% substitution. Conflict results obtained due to cement replacement by less than 15%; slight increase [17], and significant reduction [9]. Analogous effects of RB on both split tensile strength and flexural strength were observed [9, 17]. The harmful effect of RB on compressive strength is more severe in lean concrete mixes than in rich ones, for example, 30% replacement leads to a 14% reduction in the rich mix while causes a 54% reduction in the lean mix [6]. Hybrid use of both RB and fly ash reduces the harmful effect on strength [19].

Concrete immersed in sulphate solution (50 g/l Na$_2$SO$_4$) and subjected to alternative cycles of wetting and drying undergoes to a progressively reduction in ultrasonic pulse velocity; while, 20% RB substitution leads to progressively increase in ultrasonic pulse velocity in the same conditions, and maintain ultrasonic velocity in values comparable to that values of reference concrete not subjected to sulphates [20], this is a strong indicator that RB improves sulphates resistance of concrete.

The acids resistance of concrete increases due to cement replacement by RB, the compressive strength of concrete immersed for 30 days in 2% H$_2$SO$_4$ were (3, 49, 15 and 26)% more than the compressive strength of control concrete subjected to the same conditions at (10, 15, 20 and 25)% replacement respectively [18], but at the same replacement levels the compressive strength decrease significantly due to immersion in 2% NaOH for 30 days except at 15% replacement there is no change in compressive strength [18].

6. Pozzolanicity of RB

The modification of properties of cement paste, mortar and concrete was attributed to the pozzolanic contribution of RB [6, 7, 10, 15, 16, 20], moreover, Mirza et al. [5] claimed that RB possesses both pozzolanic and cementitious characteristics.

The pozzolanic reaction is a chemical reaction between silica and alumina from the SCM, on the one hand, and the calcium hydroxide resulting from the hydration of cement on the other hand, resulting in additional cementing products [21].

All allegations that RB is a pozzolanic material were not supported by conclusive evidence that the pozzolanic reaction occurred. RB was considered a pozzolanic material based on its fulfilment of the requirements of the standard specification ASTM C618 for natural pozzolan: chemical composition and SAI [5, 6]. However, the fulfilment of these requirements cannot be considered evidence of the occurrence of the pozzolanic reaction for the following reasons:

i. The percentages of silica and alumina obtained from the chemical analysis are not useful in determining the mineral composition of each, taking into account that the mineral composition is the key in determining chemical reactivity, since many forms of silica and alumina are chemically
inert and do not contribute to the pozzolanic reaction; so the British specification BS EN 197-1 [22] was more accurate when a percentage of reactive silicon dioxide was essential to the pozzolanic of material.

ii. SAI and other physical modifications may be attributed to the physical action of material particles instead of a pozzolanic reaction.

Pourkhorshidi et al. [23] concluded that: SAI is not a suitable indicator for pozzolanic activity, and the total amount of silicon dioxide, aluminum oxide and iron oxide cannot represent pozzolanic activity because the amount of amorphous minerals is the criterion; these conclusions were confirmed later by Kalina et al. [24] whose proved that ASTM C618 may shows "false positives" for inert materials, these inert materials fulfil all the requirements of specification without any pozzolanic reaction.

The definitive evidence for the occurrence of the pozzolanic reaction is the consumption of the substances involved in the reaction and formation of its products. Montmorillonite mineral is characterized by its low reactivity with Ca(OH)\textsubscript{2}, therefore, this reaction cannot consume more than 25% of montmorillonite included in it [25].

However, there are inconclusive indications of the pozzolanic reactivity of RB. Fernández et al. [26] observed chemical interaction between bentonite clay and concrete at normal temperature, the bentonite and concrete were not mixed but they contacted as two individual materials, the observations included the formation of additional C-A-S-H phase and other cementitious phases in the contact area, and these chemical interactions were stimulated by temperature rising.

The chemical reaction between RB and lime was detected by Pomakhina et al. [4] and the result of this reaction is the formation of C-S-(A)-H phases. De Windt et al. [27] studied the chemical reaction between lime and RB at 20°C and 50°C, they observed a gradual reaction between calcium hydroxide and bentonite minerals. The chemical reaction leads to:

i. A gradual decrease in bentonite minerals, portlandite and pH value, associated with

ii. A gradual increase in the formation of cementitious phases: C-S-H, C-A-S-H and strätlingite (C\textsubscript{2}ASH\textsubscript{8}).

The lime-bentonite reaction passes into three stages:

Stage I (\(\leq 1\) day), at this stage the chemical processes include: formation portlandite and start formation C-S-H, the pH ranges between 12.6 and 13.

Stage II (1-30 days), at this stage the chemical processes include: the formation of additional C-S-H, C-A-S-H and C\textsubscript{2}ASH\textsubscript{8}, and the gradual decrease in pH.

Stage III (30-100 days), at this stage the chemical processes include: gradual decalcification of C-S-H leads to decrease the Ca/Si ratio from 1.6 to 1.2, and finally 0.8, the additional formation of C-A-S-H and C\textsubscript{2}ASH\textsubscript{8}.

Furthermore, lime-RB reaction kinetics by a factor 5 due to temperature rising from 20 to 50°C; however, there is no documented evidence of such a reaction in bentonite-containing concrete.

7. Conclusions

i. Bentonite clays are a wide group that includes many types that differ in chemical and mineral composition, and physical properties.

ii. Partial replacement of Portland cement by raw bentonite leads to the following changes in the properties of cement paste, mortar and concrete:

- acceleration both initial and final setting time,
- reduce the heat of hydration,
- stiffening of consistency,
- reduce bleeding,
- increase hydration expansion,
- weaken the mechanical strength in compression, tension and flexural,
- reduce absorption,
- promote sulphates resistance and


- Increase in acids resistance.
- There are some exceptions in RB effects on the fresh and mechanical properties of paste, mortar and concrete due to bentonite type and fineness.

iii. The use of bentonite in concrete has several benefits, the most important of which are:
- reduce the cost,
- reduce cement consumption that leads to reduce environmental pollution and conservation the natural resources and
- promote durability.

iv. Currently, raw bentonite cannot be considered as an SCM because there is no conclusive evidence of its contribution to the properties of the hardened concrete through a chemical reaction.

v. Raw bentonite can be classified as inert filler until more accurate information is provided about its chemical reactivity in concrete.

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