



# Evaluation of compatibility of neutron-shielding boron aggregates with Portland cement in mortar

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## HIGHLIGHTS

- Setting time retardation of cement in mortar with boron minerals can be controlled.
- Isothermal calorimetry helps to develop optimal mix design for radiation shielding.
- The most beneficial boron-containing aggregate was boron carbide and colemanite.

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## ABSTRACT

Enhanced neutron radiation shielding capacity of protective structures can be achieved using cement-based composites with boron-containing aggregates. Experimental tests were performed to evaluate the effect of boron aggregates (colemanite, ulexite, borax, boron carbide) and nanosilica on the setting time and hydration heat of cement in mortars using isothermal calorimetry. Boron leaching test from mineral aggregates were performed in water and saturated  $\text{Ca}(\text{OH})_2$  solution. Cement setting retardation effects were found qualitatively correlated with boron leaching from mineral aggregates. A linear dependence of compressive strength of borated mortars and heat released after 72 h of cement hydration was found. A maximum content of boron compounds in mortar, allowing for a systematical control of setting time, was evaluated.

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## 1. Introduction

Current developments in the use of nuclear reactors and other advanced sources of neutron radiation require further advancement of shielding solutions. Particle spallation centers or other particle accelerators for neutron bombardment are known to generate high density neutron fluxes, e.g.  $10^{18}\text{n/s}$  like in European Spallation Source (under construction) [1]. Highly penetrating neutron radiation eventually must be captured by the shielding system to provide the necessary radiological protection for personnel and the environment. There is therefore a potential for the application of concrete of enhanced radiation shielding capacity.

Known solutions for relevant concrete mix design include special components of the mix of particular elemental composition [2,3]. Certain elements, like hydrogen, boron, cadmium, or rare earth elements, exhibit outstanding neutron shielding capacity. Considering the abundance, costs and shielding efficiency the boron containing minerals are selected as particularly desired aggregates for radiation shielding concrete. Several examples of concrete mix design containing boron-bearing compounds are given in [2] and in [4]. Because boron has a large cross-section for neutron capture, especially for the capture of thermal neutrons, its effective content in concrete can be as low as 1%. Boron compounds are known as cement setting retarders, but are only seldom used in retarding admixtures [5,6]. However, they have been recently proposed as retarding compounds both for ordinary Portland cement [7] and calcium sulfoaluminate (CSA) cement [8]. Portlandite solubility is increased on addition of boron compounds

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but in [9] it was shown that a combined effect of  $K_2O$  and  $B_2O_3$  was seen as an extension of the stability field of portlandite to much higher borate concentrations. The properties of cement required for application in radiation shielding concrete are explained in [10]. The negative impact of boron compounds on cement setting and concrete hardening should be taken into account in the radiation shielding concrete technology, [4,11–13]. This is because uncontrolled setting and hardening may induce inhomogeneity of concrete, cold joints or areas of increased porosity that would weaken the designed radiation shielding capacity. Cold joints occur when concreting procedure goes in layers and the upper layer is cast too late, i.e. after hardening of the lower layer. Instead of a full, monolithic connection between the layers a plane of weakness can be produced, therefore named cold joint. Such a weakness is not allowed in radiation shielding structures and therefore uncontrolled retardation or acceleration of concrete hardening is not acceptable. In known publications, such issue was only fragmentary dealt with.

Experimental and Monte Carlo N-Particle code (MCNP) studies on radiation shielding of boron enriched concrete demonstrated the effectiveness of some boron minerals, like colemanite, ulexite, borax, or boron products like boron-frits, boron carbide [14]. A slab attenuation experiment carried out to using  $^{252}Cf$  neutron source showed that the shielding effect of a colemanite concrete was about 1.7 times better than ordinary concrete [15]. According to Kharita [16] adding borax to concrete up to 0.5% by weight had no significant effect on strength of concrete, but it caused a significant increase of shielding efficiency in thick concrete shields, up to 80% better than unborated concrete. A neutron transport calculation of a shield containing colemanite was made by Yazar [17] using the removal-diffusion technique and the decrease in shield thickness, compared to ordinary Portland cement concrete, was determined. In spite of demonstrated benefits of boron minerals as radiation shielding compounds of concrete their effect on the durability of concrete is not well known.

The minerals are usually applied as fine grained aggregates, as recommended in [2] to achieve uniform neutron absorption characteristics of material. Boron additives of powder consistency are usually not used due to the greater potential of forming chemical solutions that act as a retarder in the concrete [18,19]. Because of contradictory effects on shielding efficiency and setting/strength properties of concrete an optimization study was performed by Yadollahi [20] that resulted in an optimal colemanite concrete mixture for thermal neutron shielding and compressive strength. The suitability of colemanite ore waste as cost-effective shrinkage-reducing agent was shown in [21]. However, this and most of other relevant shielding-related studies refer to fully hardened concrete, including also strength properties, but not the early strength and related cement hardening characteristics. The paper [13] presents isothermal calorimetry results of two type of colemanite (pure powder and ore) and their effect on cement hydration process is varied.

The aim of present study is to estimate the limits for the content of boron compounds used in cement mortars considering setting time and hydration heat of cement, as well as early mortar strength. Expecting the presence of boron to produce negative effects, an attempt was made to experimentally solve the optimization problem: finding a mix design with a maximum boron content at which setting time can be systematically controlled. The scope of the study includes four types of additives containing boron compounds.

The criterion of maximum boron content is assumed here as a technically justified simplification for mortar mix design for enhanced shielding capacity. Exact and final evaluation of the radiation shielding is normally carried out on whole structure when both the elemental composition of the material and the shape and dimensions of the structure influence the shielding efficiency

## 2. Experimental

### 2.1. Materials and specimens

The measurements were made on cement mortar samples with constant water to cement ratio  $w/c = 0.5$ , modified by addition of boron containing aggregate. The following materials were used:

- ordinary Portland cement CEM I 42.5 R (EN 197-1:2011), Table 1,
- deionized water,
- sand for testing of cement strength complying with EN 196-1:2016 [22],
- fine grained boron-containing aggregates:
  - a) colemanite with grain size 0.5–2 mm ( $Ca_2B_6O_{11} \cdot 5H_2O$ , content of B = 15.78 wt%),
  - b) ulexite with grain size 0.5–2 mm ( $NaCaB_5O_9 \cdot 5H_2O$ , content of B = 13.34 wt %),
  - c) sodium tetraborate pentahydrate (borax) with grain size 0–1.6 mm ( $Na_2B_4O_7 \cdot 5H_2O$ , content of B = 14.85 wt%),
  - d) boron carbide with grain size 90–125  $\mu m$  and 94% of purity ( $B_4C$ , content of B = 73.56 wt%, take into account the purity of the raw material),
- amorphous nanosilica with grain size  $\leq 30$  nm ( $nSiO_2$ ) as water dispersion.

For heat of hydration measurements, mortar samples were prepared using the following mass ratios: cement:water:sand 1:0.5:0.75. At these proportions, the binder's volume share is 44% – it was intentionally high to extract a strong signal of the hydration heat generated. The additive, in the form of mineral or synthetic boron aggregate, was used as a partial replacement for quartz sand. The target content of boron in aggregates was from 2 to 10% per cement mass. This could not be achieved for borax and ulexite because of significant setting delay, therefore the range of boron content was diminished down to 0.33% and 1% of boron per cement mass, respectively. For  $B_4C$  this range was increased up to 40% B per cement mass because of weak influence on cement setting and hardening characteristics. As an additive for selected mortars, an amorphous nanosilica in form of an aqueous dispersion was added in an amount of 1 and 2% per cement mass; water present in the dispersion was taken into account by correction the amount of water added.

### 2.2. Test methods

An isothermal calorimetry method was used for the determination of progress of the cement hydration in Calmetrix I-Cal 2000 HPC isothermal calorimeter at the temperature of 23 °C for 72 h. The ASTM C 1679 [23] standard was used to interpret the results. The compressive strength of mortar specimens was determined according to the standard EN 196-1 on  $40 \times 40 \times 160$  mm prisms. The strength was determined after 72 h and after 28 days of hardening under standard conditions of constant temperature  $20 \pm 2$  °C and high humidity  $RH > 95\%$ . Boron leaching test from mineral aggregates was performed to determine the concentration of boron in solutions obtained by shaking mixtures of aggregates (colemanite, ulexite, borax) with solvent (water or saturated  $Ca(OH)_2$  solution) at solid/liquid ratio 1:10. Shaking was carried out at 23 °C for 3, 6 and 24 h. Boron concentration was determined by ICP-MS method using Agilent 7700x from Agilent Technologies, following [24]. Each measurement was repeated six times.

## 3. Test results

The rate of heat release during cement hydration in mortars with additives is shown in Fig. 1a–f. The content of the additive is indicated as the ratio of boron mass to cement weight. Ulexite

**Table 1**  
Properties of cement CEM I 42.5R (EN 197-1:2011).

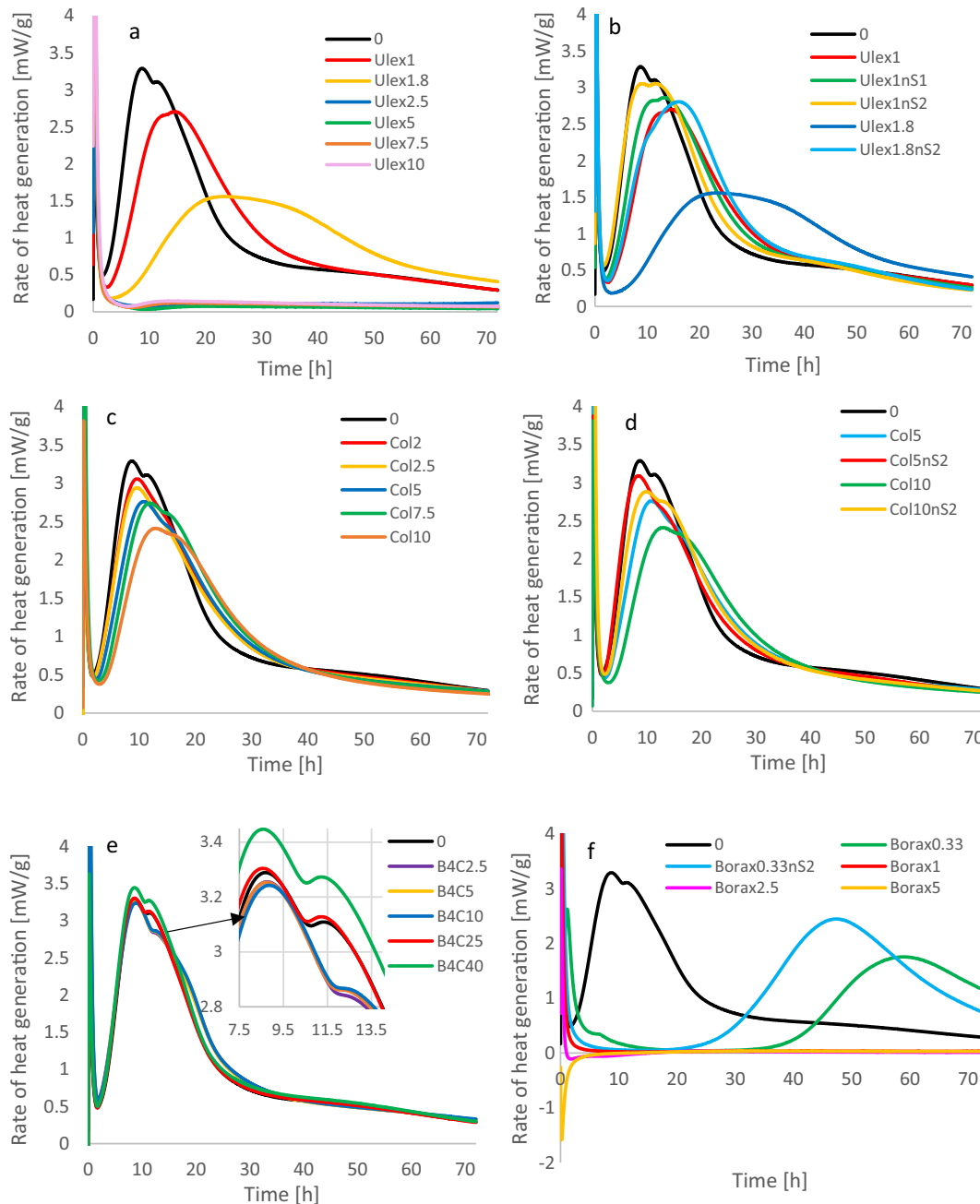
Compressive strength	Unit	Value	Requirement
After 28 days	MPa	59.1	$\geq 42.5$ $\leq 62.5$
Physical properties	Unit	Value	Requirement
Initial setting time	min	172	$\geq 60$
Water to the standard consistency	%	28.4	No requirements
Soundness	mm	0.3	$\leq 10$
Specific surface area (Bleime method)	cm <sup>2</sup> /g	4000	No requirements
Chemical composition	Unit	Value	Requirement
Loss on ignition	%	3.11	$\leq 5.0$
Insoluble residue		0.69	$\leq 5.0$
Sulphates as $SO_3$		2.81	$\leq 4.0$
$Cl^-$		0.084	$\leq 0.10$
$Na_2O_{eq}$ ( $Na_2O + 0.658 K_2O$ )		0.70	No requirements

aggregate greatly influenced the process of cement hydration, Fig. 1a. At a content of 1% B, it moved the calorimetric curve to a longer hydration time and reduced the rate of heat generation. Increasing the content of ulexite to 1.8% of B resulted in even stronger changes. On the other hand, at 2.5% B and higher, the material showed no setting within 3 days, resulting in flat curves in the graph. After removal from the calorimeter, the samples were still soft. After a few weeks in the lab the samples hardened, but they could be easily crushed with fingers.

Nanosilica addition in the form of an aqueous dispersion was used to improve the cement setting rate with this type of aggregate. Obtained calorimetric curves are shown in Fig. 1b. The use

of nanosilica reduced the severe retardation caused by the addition of ulexite.

The graphs in Fig. 1c illustrate the effect of colemanite content in mortar: from 2 to 10% of boron per unit of cement mass. A delay in hydration process and a decrease of the hardening rate with the increase of colemanite content is seen. Compared with reference mortar, the maximum rate of heat generation is also reduced. The use of nanosilica, as in the case of ulexite, improved the cement hydration process (Fig. 1d). As the amount of nanosilica increased, the hydration process accelerated. It was also found that the maximum hydration rate per gram of cement was increased with the addition of nanosilica.



**Fig. 1.** The rate of heat generated per 1 g of cement during hydration of cement in mortar with different contents of (a) ulexite, (b) ulexite and nanosilica, (c) colemanite (d) colemanite and nanosilica, (e) boron carbide, (f) borax and nanosilica. Assumed notations: 0 – mortar without addition of boron-containing aggregate, in the other samples the following scheme was used: name of aggregate, the first number – % of boron content in relation to cement mass in mortars, nS – addition of nanosilica, the second number – % of nanosilica content in relation to cement mass in mortars (e.g. Ulex1nS1 denotes mortar specimen with 1% of boron per cement mass in the form of ulexite and 1% of nanosilica per cement mass).

Boron carbide – up to 40% B – did not significantly change the hydration rate of cement, as it was in the case of ulexite and colemanite. As shown in the enlarged fragment of Fig. 1e, with an increase in B<sub>4</sub>C content some increase in the maximum rate of heat generation was observed.

The effect of the addition of fine-grained borax, replacing a part of quartz sand, in the range of 0.33 to 5% B, is shown in Fig. 1f. On the calorimetric curves, borax mortar showed no setting. Samples of mortar removed from the calorimeter after 3 days were not hardened. At a content of borax of 5% B the process was initially endothermic (the heat was absorbed instead of emitted), then the graph was flat and oscillated around zero. With the addition of 1 and 2.5% B, the process was initially exothermic, after 2–3 h the graph ran flat at zero. Evidently the use of borax in this amount has stopped the cement hydration process. For comparison purposes, the isothermal calorimetry test was performed at a borax content of 0.33% B and 0.33% B with 2% of nanosilica. The results are shown in Fig. 1f. Despite such a small addition there was a very long delay in hydration of cement. The addition of nanosilica reduced this difference, however, compared to the reference setting time, this change was negligible. As even very small amounts of boron gave large delays in cement hydration, no further studies on the use of borax were made.

Following standard recommendation of ASTM C1702 isothermal calorimetry tests were run in duplicates [25,26]. Fig. 2 shows examples of repeatability of calorimetric curve shapes. The repeatability was good. Differences in shapes and coordinates of

characteristic points in the curves were in accordance with standard description.

The total heat released per 1 g of cement was calculated as the area under the heat-rate curve. Due to initial process disturbances, resulting from mixing of cement and water outside the calorimeter, the heat generated during the first 90 min was omitted, as suggested in [25]. Fig. 3 shows the relationship between the total heat generated per 1 g of cement and the content of boron in the aggregates.

The amount of heat generated during cement hydration in mortar varies depending on the boron additive used. With an increase of colemanite content, a slight decrease in the amount of heat generated is noticeable, reaching up to 12% at 10% of the B content. In the case of ulexite, the changes are much more pronounced. The addition of 1.8% B decreases the amount of heat released, and above 2.5% B the heat released decreases significantly due to lack of setting. The addition of boron carbide does not significantly affect the amount of heat generated. A slight increase in the heat generated is seen with B content increase, up to 5% at 40% B. Even a small addition of borax of 0.33% B reduces the amount of heat released by 35%. The use of nanosilica in all cases increased the amount of heat released (Fig. 3b). The increase was from 4.4% to 48%. The biggest increase occurs with the addition of borax.

Results of the compressive strength test and the corresponding amount of heat of hydration from calorimetric measurements are shown in Table 2. The determination of strength after 72 h of hardening was justified by the intention to find a correlation between the strength and the amount of heat released during this time in the isothermal calorimeter test.

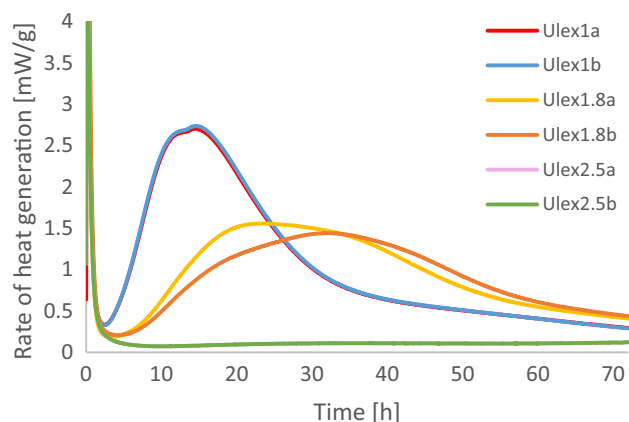


Fig. 2. Illustration of repeatability of calorimetric curves for selected pairs of specimens.

Table 2

Compressive strength of mortars after 72 h and 28 days and total heat of cement hydration generated during 72 h in isothermal calorimeter test at 23 °C.

Mortar composition	Total heat generated during 72 h [J/g]	Compressive strength [MPa]	
		after 72 h of hardening	after 28 days of hardening
0	266.0	25.4 ± 0.8	48.4 ± 2.5
OnS2	287.3	31.0 ± 1.7	45.6 ± 0.9
Ulex1.8	228.3	10.3 ± 0.6	39.1 ± 2.5
Ulex1.8nS2	274.5	26.5 ± 1.4	40.0 ± 2.5
Kol5	248.6	20.8 ± 0.2	34.7 ± 1.7
Kol5nS2	259.6	25.1 ± 0.7	39.2 ± 0.1
B4C5	275.2	24.3 ± 0.6	41.1 ± 1.3
B4C10	277.6	28.4 ± 1.2	44.5 ± 3.0
Borax0.33	172.4	1.1 ± 0.6	29.1 ± 2.7

\* Specimen designation as in the figures.

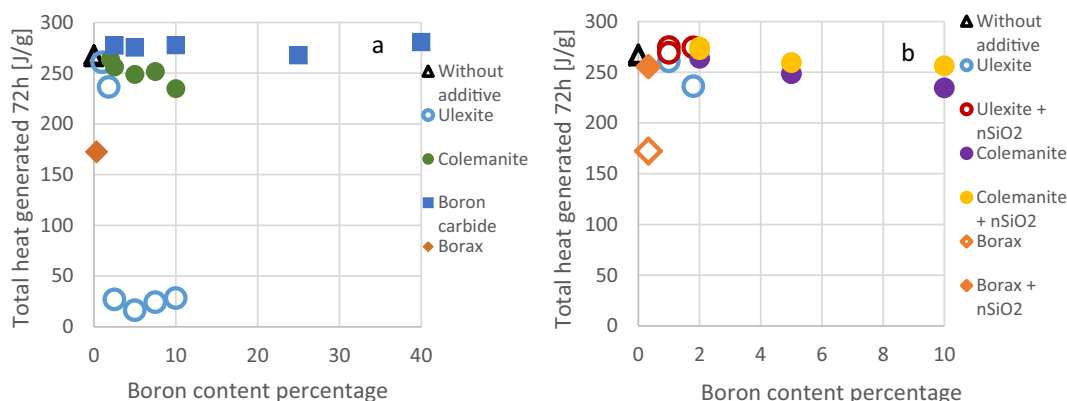


Fig. 3. Total heat generated within 72 h of hydration per 1 g of cement as a function of boron content in aggregates (expressed in% by cement weight) for mortars without (a) and with addition (b) of nanosilica.

Table 3 shows the result of boron leaching test in  $H_2O$  and  $Ca(OH)_2$  saturated solution. The lowest boron content was found for colemanite aggregate, it was twice as high for ulexite aggregate, and a factor 10 higher for borax. In most cases, an increase of boron content was observed along with increasing leaching time, only for borax in  $Ca(OH)_2$  solution such trend was in the reverse direction. During 3 and 6 h of leaching the boron content was higher in  $Ca(OH)_2$  solution than in water by a factor up to 1.5. At 24 h it was still larger for colemanite by a factor of 1.3, but for ulexite and borax the boron content in water was higher than in lime solution by 10–20%. The relevance of leaching results to support explanation of the cement setting delay is discussed in the following chapter.

## 4. Data analysis and discussion

### 4.1. Setting time

The compatibility assessment between boron containing aggregates and Portland cement was based on cement setting time and early strength of mortar. The initial and the final setting time was evaluated using the characteristic points of calorimetric curves as proposed by Ge et al. [27] and Bobrowicz [28] (Fig. 4). Authors of the first article proposed to calculate the first derivative of the function of the heat power in time. At the point at which the first derivative reaches its maximum, the increase in the rate of heat generation is the highest and is defined as the initial setting (Fig. 4a). On the calorimetric curve two straight lines, tangent to the minimum and tangent to the point of inflection, are drawn by Bobrowicz [28], and the point of their intersection is defined as the initial setting (Fig. 4b). The results of determination of the initial setting time are shown in Figs. 5 and 6 for mortars contain-

ing boron aggregates as a function of B content in relation to the mass of cement.

The initial setting time determined by both methods varies considerably. Referring to the time determined by the Vicat method for reference mortar – 169 min (2.8 h), quite satisfactory result obtained by method II can be found. Both figures show qualitatively similar effects of boron additives. In the case of ulexite and colemanite, the increase in initial setting time increases with the increase in of boron content. Only two values are shown in the mortars with ulexite, 1 and 1.8% B, due to lack of sufficient setting at higher contents (2.5–10% B). A linear increase of the extension of the initial setting time with the increase of boron content in mortar is apparent in the case of colemanite aggregates.

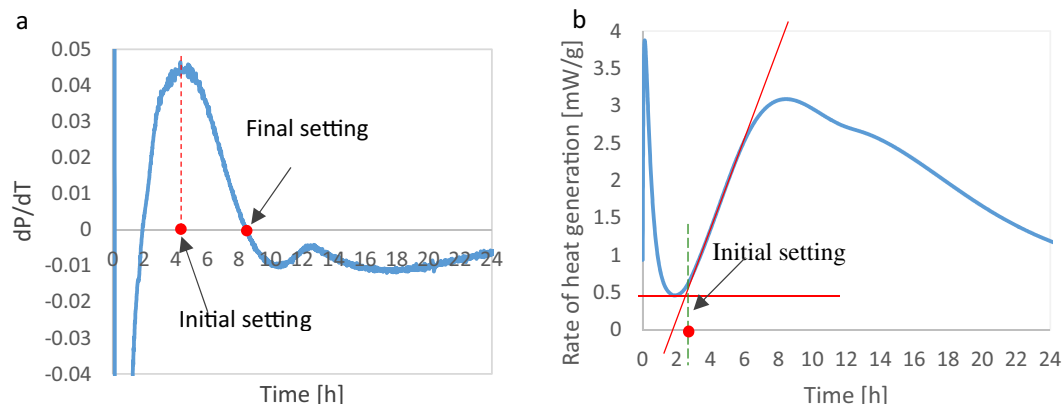
The initial setting time of cement in boron carbide mortar is practically unchanged with increasing  $B_4C$  content. The results of the setting time with 0.33% B in the form of borax are not shown in the figure, due to the very long delay (34.5 h by method I and 39 h by method II). For higher borax content, the cement setting was completely stopped. Figs. 5b and 6b show the effect of nanosilica addition on the initial setting time of mortar with ulexite and colemanite. In each case, nanosilica as a source of new nucleation sites accelerates the hydration process. There is a faster start of setting compared to the same mixtures without the addition of nanosilica.

Partial replacement of standard sand in mortars by boron containing aggregates induced a decrease of mortar consistency, particularly in the case of ulexite and borax. It was observed that addition of nanosilica also made it more difficult to mix mortar ingredients. For this reason, the Vicat method, which is a standard test adequate for cement paste of normal consistency, was not used in this investigation. Changes in the consistency of the mortar, requiring increased mixing energy, can influence the differences of the rate of heat generation during cement hydration. These effects were described by Wadsö [25,29] mixing at higher intensity shifts hydration peak to earlier times. However, conducted comparative tests with manual mixing by two operators did not show significant differences, only 1–2% difference in maximum hydration heat generation rate.

**Table 3**

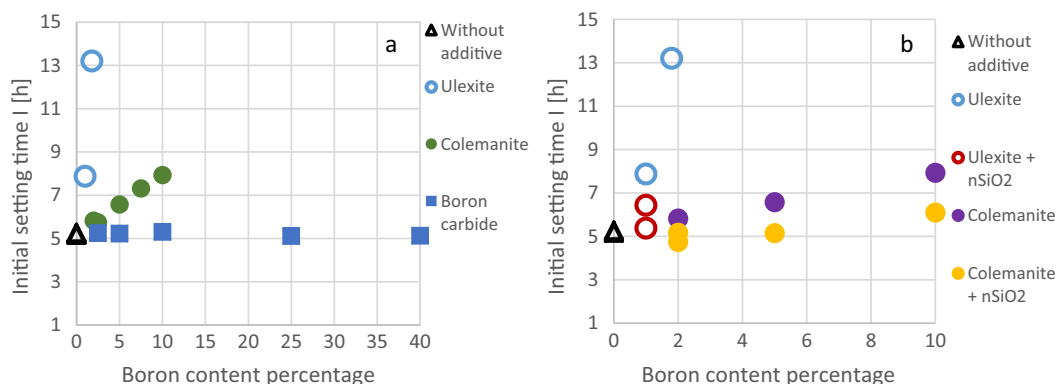
Boron content in solutions after shaking colemanite, ulexite and borax in water or saturated  $Ca(OH)_2$  solution for 3, 6 and 24 h. Solid/liquid ratio = 1:10. Temperature 23 °C.

Fine aggregate	Liquid	Boron content [mg/dm <sup>3</sup> ]		
		3 h	6 h	24 h
colemanite	$H_2O$	243 ± 61	237 ± 59	405 ± 101
ulexite	$H_2O$	367 ± 91	505 ± 126	992 ± 248
borax	$H_2O$	3037 ± 759	3183 ± 796	2962 ± 741
colemanite	$H_2O + Ca(OH)_2$	278 ± 70	282 ± 71	522 ± 131
ulexite	$H_2O + Ca(OH)_2$	567 ± 142	629 ± 157	870 ± 218
borax	$H_2O + Ca(OH)_2$	3647 ± 911	3032 ± 758	2418 ± 604

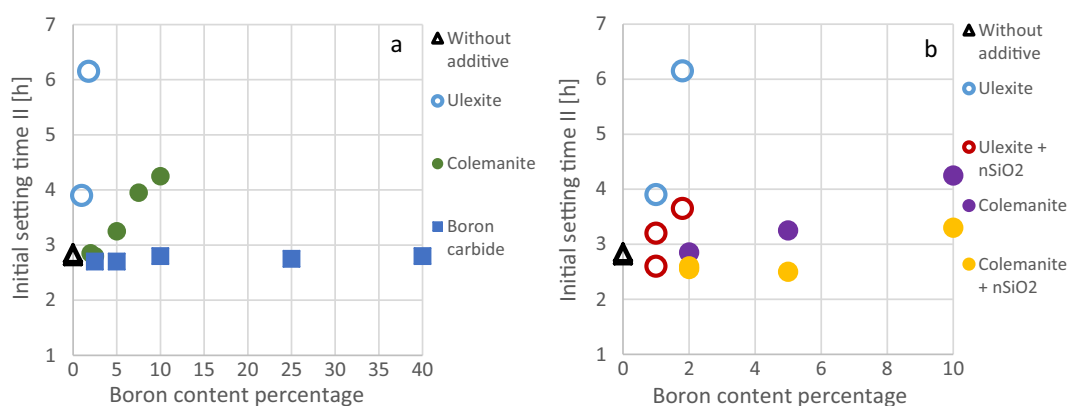


**Fig. 4.** Two concepts of the initial setting time determination: (a) the first derivative of the function of the rate of heat generation in time [27] (b) the point of intersection of tangent to the minimum and tangent to the point of inflection [28].





**Fig. 5.** Initial setting time determined by method I (the first derivative) as a% of boron content in relation to cement mass in mortars without (a) and with addition (b) of nanosilica.



**Fig. 6.** Initial setting time determined by method II (intersection of tangents) as a% of boron content in relation to cement mass in mortars without (a) and with addition (b) of nanosilica.

with  $R^2 = 0.95$ . The effect of differentiation of aggregates is not clearly visible due to differences in aggregate content and presumably dominant influence of paste porosity on early strength of cement mortar. The strength of mortar after 28 days of hardening was reduced by the use of boron-containing aggregates in relation to the reference mortar. The smallest decrease (by about 10–20%) in 28-day strength was caused by boron carbide aggregates, the largest decrease (about 40%) was found for borax addition, despite its use in a very small amount.

#### 4.3. Boron leaching

Determination of boron content in  $H_2O$  and  $Ca(OH)_2$  saturated solution allowed for calculation of relative leached boron content. Considering a proper content of B in three boron-containing minerals the percentage of leached boron content is shown in Table 4. From 18 to 27% of boron was leached from borax and in this case the leaching was not significantly changed in time in water. However it decreased by one third at 24 h in  $Ca(OH)_2$  solution. For colemanite and ulexite the boron leaching was clearly increasing in time showing the opposite trend than for borax. At 3 h the boron leaching from colemanite was about 13–14 times lower than for borax and 1.8–2.5 times lower than for ulexite.

Boron leaching test results in saturated solution of  $Ca(OH)_2$  (Table 4) show some similarity with the initial setting time of cement in borated mortars. The most boron is leached from borax, and the least from colemanite; similarly with the setting time it was observed that the greatest delay of the setting time was caused by borax, and the smallest by colemanite. An addition of

a small amount of highly soluble borax (0.33% B) extended the initial set time from 2.8 h to 39 h, and in greater quantities inhibited setting and hardening of cement. The effect of ulexite addition was also significant: at the content of 1.8% B the initial setting time was delayed up to 6 h and at 2.5% B the setting was inhibited. Observed trends indicate that effects of boron-containing minerals on initial setting time of cement can be qualitatively explained considering boron leaching.

The mechanism of changes in the properties of cement mortars caused by the presence of boron compounds has not been explained satisfactorily to date. It is suggested that inhibition of cement hydration attributed to borates could arise from surface adsorption and possibly formation of protective layers over the cement grains due to precipitation with calcium [19,31–34]. As suggested, a cause of retardation of cement setting time and the

**Table 4**

The percentage of boron calculated relative to its content in the starting material that passed to the solution by shaking colemanite, ulexite and borax in water or saturated  $Ca(OH)_2$  solution. Solid/liquid ratio = 1:10, temperature 23 °C.

Mineral aggregate	Liquid	Weight% of boron in solution		
		3 h	6 h	24 h
colemanite	$H_2O$	$1.5 \pm 0.4$	$1.5 \pm 0.4$	$2.6 \pm 0.6$
ulexite		$2.8 \pm 0.7$	$3.8 \pm 0.9$	$7.4 \pm 1.9$
borax		$20.5 \pm 5.1$	$21.4 \pm 5.4$	$20.0 \pm 5.0$
colemanite	$H_2O + Ca(OH)_2$	$1.8 \pm 0.6$	$1.8 \pm 0.6$	$3.3 \pm 0.8$
ulexite		$4.3 \pm 1.1$	$4.7 \pm 1.2$	$6.5 \pm 1.6$
borax		$24.6 \pm 6.1$	$20.4 \pm 5.1$	$16.3 \pm 4.1$

slow strength development, and sometimes the total inhibition of these processes, is due to the formation on cement grains a thin layer (film) that blocks water access to the most active cement components, alite –  $3\text{CaO} \cdot \text{SiO}_2$  and tricalcium aluminate –  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ . It is assumed that this film is an amorphous hydrated calcium borate [32,33]. The processes occurring on the surface of  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  grains, especially the formation, growth and stability of ettringite  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$  have a major influence on the beginning of setting. The presence of a passive calcium borate film on the surface of  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  could slow down or inhibit its hydration, extending the setting time of the cement.

The increase in strength of Portland cement mortars during the initial 28 days is determined by the hydration rate of alite, of which the hydrated products same as the hydrated products of belite are calcium hydroxide and quasisamorphous calcium silicates, denoted as C-S-H [35]. Suggestions to explain the mechanism of limiting the hydration rate of calcium silicates (alite and belite) in the presence of boron in the same way as limitations of hydration progress of  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  (protective layers), do not seem appropriate, because the reduction in the hydration rate of calcium silicates is already observed at very low content boron in their structures [36]. It seems that the reasons are C-S-H changes resulting from the limitation of the polycondensation rate of silicon-oxygen anions due to the presence of borate ions.

#### 4.4. Nanosilica effects

Although boron containing minerals may influence the early hydration of cement by different mechanisms, the assumed methodology of calorimetric studies allowed to demonstrate the beneficial role of nanosilica to neutralize the observed setting delay. Nanosilica effects have not yet been quantified in this case. According to [37,38], the role of nanosilica is to act as nucleation sites and react with ingredients of the cement paste to form additional nuclei (C-S-H) and it causes increase in hydration speed. The significance of the surface area of filler on the kinetics of hydration was shown in [39,40]. The beneficial effect of nanosilica is also experimentally demonstrated by the strength of the mortar in the first 72 h of hydration. In addition to the already mentioned effect of nanosilica on the hydration of Portland cement, it should be noted that nanosilica nanoparticles will react very quickly with  $\text{Ca}(\text{OH})_2$  and will bind the boron ions present in the solution thus limiting the impact of borates on the hydration of  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  thereby on beginning of cement setting time.

#### 4.5. Boron carbide and borax effects

The applicability of calorimetric methods for studying effects of retarding admixtures on cement hydration in paste specimens is known from [6,19,41,37,42]. However, the isothermal calorimetry tests on mortars allowed to demonstrate the beneficial role of boron carbide fine-grained aggregates. It allows for obtaining high boron content in the elemental composition of mortar, without negatively affecting the setting time. The effect of  $\text{B}_4\text{C}$  on the compressive strength of mortar proved to be beneficial. Similar effects on strength are known from Nabilah paper [43]. However, the technical benefits of using  $\text{B}_4\text{C}$  have to be judged by its high cost justifying its use in exceptional cases.

It is known from the literature that borax was used in neutron radiation shielding materials, but only in a very small quantities. According to [16] the addition of less than 0.5% by weight of borax per unit mass of concrete did not significantly affect to the setting time and strength of the concrete. The amount of pure boron provided in this way is negligible, and according to the proportion used in our research, it is 0.17% B per unit of cement mass. The highest borax content used by the authors of the cited article

was 1% (0.33% B per unit of cement mass). However, from our comparative studies, with the same amount of borax, it follows that even such a small amount of additive causes a significant delay in cement setting time. Wadsö et al. also noticed a strong cement hydration delay after the addition of borax [13].

#### 4.6. Radiation shielding

It is known from the literature that boron, particularly  $^{10}\text{B}$ , has a very high absorption capacity for thermal neutrons [2–4]. Boron has high cross section for neutron capturing and its use in concrete makes it possible to capture neutrons without producing secondary gamma rays of high energy. In [44] the tests on radiation transmission of concrete including boron compounds were reported for gamma rays. Mass attenuation coefficients were found to increase linearly with increasing boron concentration in concrete. Therefore, in spite of the lack of direct shielding experiments, the obtained results are considered adequate for materials design for radiation shielding.

### 5. Conclusions

The following conclusions can be drawn from the performed investigation.

1. A significant effect of the content of boron-containing aggregates on the delay of initial and final setting time as well as on the decrease of heat rate generated during cement hydration was found. The effects were very different for different types of boron additives, in extreme cases the setting of Portland cement was inhibited.
2. The most beneficial boron-bearing mineral aggregate was colemanite, allowing for significantly increased boron content in mortar without much influence on the hydration process. Borax and ulexite aggregates in larger quantities inhibited the cement hydration process, the material did not set after 72 h at 23 °C.
3. The use of synthetic boron-containing material  $\text{B}_4\text{C}$  as quartz sand replacement addition up to 40% of B per cement mass did not change the kinetics of setting and early hardening of cement.
4. The addition of colemanite aggregate corresponding to the content of boron of 10% by cement mass resulted in the initial and final setting time delay of 4.25 and 12.9 h, respectively.
5. Boron-induced delay of cement hydration can be effectively modified with addition of nanosilica. With the content within 1–2% of cement weight, the hydration process was significantly accelerated, eliminating the delay caused by the colemanite and ulexite aggregate. With the addition of borax, even in the smallest amount used, such addition of nanosilica did not significantly counteract the cement setting delay.
6. The boron leaching tests on mineral aggregates in  $\text{H}_2\text{O}$  and  $\text{Ca}(\text{OH})_2$  saturated solution revealed the lowest boron content for colemanite aggregate and the highest for borax. The mass of leached boron in saturated  $\text{Ca}(\text{OH})_2$  solution for colemanite, ulexite and borax was in the respective proportion of 1:2:15.
7. The compressive strength of mortars containing boron aggregates determined after 72 h of hardening was linearly correlated with the amount of heat released after 72 h of hydration determined by isothermal calorimetry.
8. The observed linear relationship between the hydration heat generated and compressive strength, and the logical effects of the delay in initial and final setting time allow for the isothermal calorimetry method to be used as compatibility assessment tool for boron containing aggregates. It can be a convenient tool as it requires a small amount of material and is highly repetitive.

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