Fire properties of borated polyethylene

Madsen, Dan; Van Hees, Patrick; Jörud, Fredrik

Published in:
Fire and Materials 2015 - 14th International Conference and Exhibition, Proceedings

2015

Fire properties of borated polyethylene

Dan Madsen, Grontmij AB, Sweden
Patrick van Hees, Lund University, Sweden
Fredrik Jörud, ESS AB, Sweden

ABSTRACT

This work has been made as a thesis for a BSc degree in Fire Protection Engineering at Lund University. The work has been supported and funded by ESS AB, European Spallation Source, in Lund. ESS AB is a publicly held company, owned by Sweden and Denmark as host countries. These host countries, together with at least 17 other European countries, will build and establish a multi-disciplinary research center just outside of Lund. The research will be based on the world's most powerful neutron source and be 30 times brighter than the leading active facilities today. The scope and objective of this work was to evaluate and determine fire properties for a material that will be used for radiation shielding at the Research center. Traditionally two materials, borated paraffin and borated polyethylene, are used for radiation shielding at neutron-based research laboratories. Since base paraffin and base polyethylene are known as combustible materials with a high-energy content, it is of great interest to determine the actual fire properties of the borated versions. As the application of the borated paraffin will be in encapsulated blockhouse wax walls of steel, the prioritized objective in this paper was to evaluate the borated polyethylene that was initially considered to be used as unprotected sheets for radiation shielding. The borated polyethylene was bought at a global supplier of plastic products. Some current building regulations together with valuable information concerning the material were also discussed. The results of the work are based on literature research, interviews, discussions and test methods (cone calorimeter tests, parallel panel tests and combustion under an exhaust hood). Limitations of the work are that it does not consider toxicity, smoke production or a measured heat release rate in the full scale tests. The Euroclass classification according to *European fire classification of materials, construction products and building elements* was only in the application as a construction product or surface lining and not as flooring.

The evaluation of borated polyethylene shows that the fire properties vary depending on the orientation of the material. When burning in a horizontal orientation the Boron oxide establish a suffocating residue layer that dampens the release of pyrolysis gases but in vertical orientation the Boron oxide runs off with the melted material and does not form a suffocating residue layer. When burning in vertical orientation the borated polyethylene also has burning droplets. Values obtained in cone calorimeter tests were used in a screening method, Conetools, to determine the borated polyethylene as D-classified material according the Euroclasses by the European fire classification of materials, construction products and building elements. The actual classification and the burning droplets demands fire protection measures in most building classes according a simplified design by the Building Regulations of the Swedish Board of Housing, Building and Planning, BBR.

Future work to ensure a safe use of combustible materials for radiation shielding should be to verify the actual applications of fire protections measures. This verification is strengthened in the guideline BFS 2013:11 chapter 3.4 Skyddad brandenergi (Swedish). Further on in the future it would be interesting to develop a new material for radiation shielding that can be used as self-supporting building elements with fire properties that does not demand fire protection measures or extended fire protection systems.

INTRODUCTION

This work is made as a thesis at ESS AB, European Spallation Source, in Lund Sweden. Background to the work was a request for an evaluation of fire properties for paraffin and polyethylene materials with boron content that are suggested to be used in large quantities for radiation shielding at the new research center in Lund. The work started initially as an internship during the summer and resulted in the report *Fire properties of Paraffin, Borated paraffin, Polyethylene, Borated polyethylene* [1].
In this work the primary objective has been on a polyethylene-based material with a 5% Boron content. Evaluating obtained data and information from literature research, laboratory tests, calculations and communication with and visit at suppliers made the work. Test methods were the cone calorimeter tests [2], a Parallel panel test inspired by FM GLOBAL [3] and burning the material under an exhaust hood. Calculations in Conetools [4] were made to predict fire properties according to Single Burning Item test EN 13823, SBI, and the Room Corner Test ISO 9705, RCT, from the results achieved in the cone calorimeter tests. The Parallel panel test was made to make qualitative determination of how the material, in a vertical orientation, reacts as it is exposed to heat and fire. Combustion under an exhaust hood was made to receive values in order to calculate and determine the Smoke potential of the material.

Scope and objectives

The scope of this work was to evaluate fire properties, applications and some regulations that concern a material suggested for radiation shielding at ESS AB. The primary objective was to determine applicable parameters for modeling and understanding a design fire with a polyethylene-based material with a Boron additive.

Company

ESS AB is a publicly held company, owned by Sweden and Denmark, which will together with 17 other European partner countries, build and establish a multi-disciplinary research center in Lund. It will be based on the world's most powerful neutron source and be 30 times brighter than leading facilities today [5]. The Research center will deliver the first neutrons in 2019 [6].

Radiation shielding

The neutrons that are produced for research which do not make it to the experiments have to be eliminated, as they are sources of background radiation and potential errors. For slowing down and stopping neutrons it has been shown that materials with a high content of hydrogen atoms are very effective. In addition there are many of these materials that are relatively inexpensive. Materials such as borated paraffin and borated polyethylene are commonly used in several research centers in Europe that have research based on neutrons. The materials are used in different applications, paraffin is molded in steel blockhouse wax building elements as the paraffin is not self-supporting enough by itself to form self-supporting wall elements. Polyethylene is used in sheets and can form self-supporting building elements. The advantages of using these effective materials are that they are space saving, more flexible and have a relatively low density.

Borated paraffin and borated polyethylene are suggested for use in high quantities as materials for shielding of neutron radiation at ESS in Lund. Both materials are also known to have a high effective heat of combustion when they are burning as the base material without the boron additive, namely paraffin wax = 43,1 kJ/g and polyethylene = 43,1-43,4 kJ/g [7]. For optimal radiation shielding, the materials are mixed with Boron (B), element atomic number 5, as a Boric acid additive in paraffin and as a Boron oxide additive in polyethylene. The boron additive also results in a higher melting point and fire retardant properties [8], which is positive from a fire safety point of view. The molecular formulas for the boron additives are $B(OH)_3$ for Boric acid and B_2O_3 for Boron oxide. Melting points for the additives are: 171°C for Boric acid and 450 °C for Boron oxide [9] which is higher than for paraffin, 65-70 °C, and polyethylene, 135 °C.

In order to design a sufficient radiation shield that is also acceptable from a fire safety point of view it is of great interest to know the materials properties as they are exposed to heat and fire. Important properties to have knowledge about are melting point, time to ignition, ignition temperature, fire growth rate, heat release rate, effective heat of combustion, mass loss rate, smoke potential and critical irradiance. These fire properties can make a base for classification.

METHODS

Test methods were the cone calorimeter tests according to ISO 5660 [2], a Parallel panel test inspired by FM GLOBAL [3] and burning the material under an exhaust hood.

BUILDING CODES

The building of the new research center has to relate to the European and Swedish regulations. This work addresses especially the European fire classification of materials, construction products and building elements [10] and the Swedish Building Regulations [11], together with a common advice in the guideline BFS 2013:11 – BBRBE 1 by the Swedish National Board of Housing, Building and Planning [12], which puts a larger responsibility on the verification of fire protection measures.

RESULTS

The content of this paragraph handles a common advice from the Swedish National Board of Housing, Building and Planning and results from tests performed on the borated polyethylene.

BFS 2013:11 – BBRBE 1, 3.4 Skyddad brandenergi

The general advice in the guideline BFS 2013:11 – BBRBE 1 by the Swedish National Board of Housing, Building and Planning, puts a larger responsibility on the verification of fire protection measures. Fire protection measures should be verified by relevant literature or experiments. At the time of this work there were no such relevant literature or experiments found that from a fire safety point of view verified a safe use of building elements that exist of/or contains borated paraffin/polyethylene.

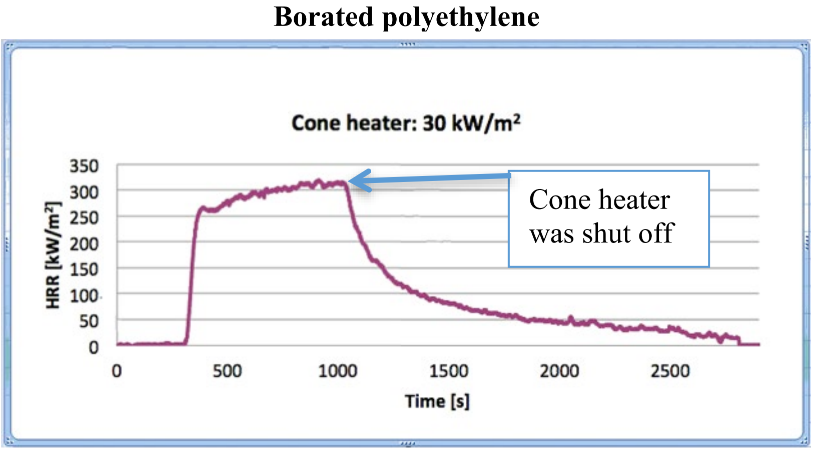
Borated polyethylene

Following properties of borated polyethylene are retrieved from tests, data sheets, calculations and determination by software tools.

Self-extinguish test

In the self-extinguish test, the material was ignited and the cone heater was shut off after 18:36 minutes (min:sec). The fire retardant properties are visually shown in Figure 1 where the heat release rate decreases as soon as the imposed radiation is shut off.

Figure 1: Chart of self-extinguish test.



Critical irradiance and thermal inertia

The theoretical critical irradiance of ignition, $\dot{q}''_{cr}$, according to Janssens [13] is presented in Table 1 as well as the thermal inertia according to Hopkins [14] where T_{ig} is assumed to be 280 ºC. The assumptions for T_{ig} are roughly validated in cone calorimeter tests. R^2-value describes the best fit correlation to obtain $\dot{q}''_{cr}$.

Table 1

Material	$\dot{q}''_{cr}$ [kW/m^2]	Thermal inertia [kJ^2/m^4•K^2•s]	R^2 [-]
Borated polyethylene	7,4	2,4	0,996

Heat release rate and effective heat of combustion

Peak results of Heat Release Rate, HRR, and effective heat of combustion are presented in Table 2.

Table 2

Irradiance [kW/m2]	Peak HRR/m^2* [kW]	Effective heat of combustion [kJ/g]
30	454	37,7
40	590	37,9
50	707	38,4

* Average of the 10 highest values in 3 tests for each irradiance level.
The value of each test is based on an average of the 10 highest measurements.
The value at each irradiance level is initially based as an average of 3 repeated tests.
Any spill is excluded in the calculation of effective heat of combustion. An average Effective heat of combustion was determined as 38 kJ/g.

Mass loss rate

Results in Table 3 are average values of the 10 highest values within each of 3 repeated tests at each irradiance level.

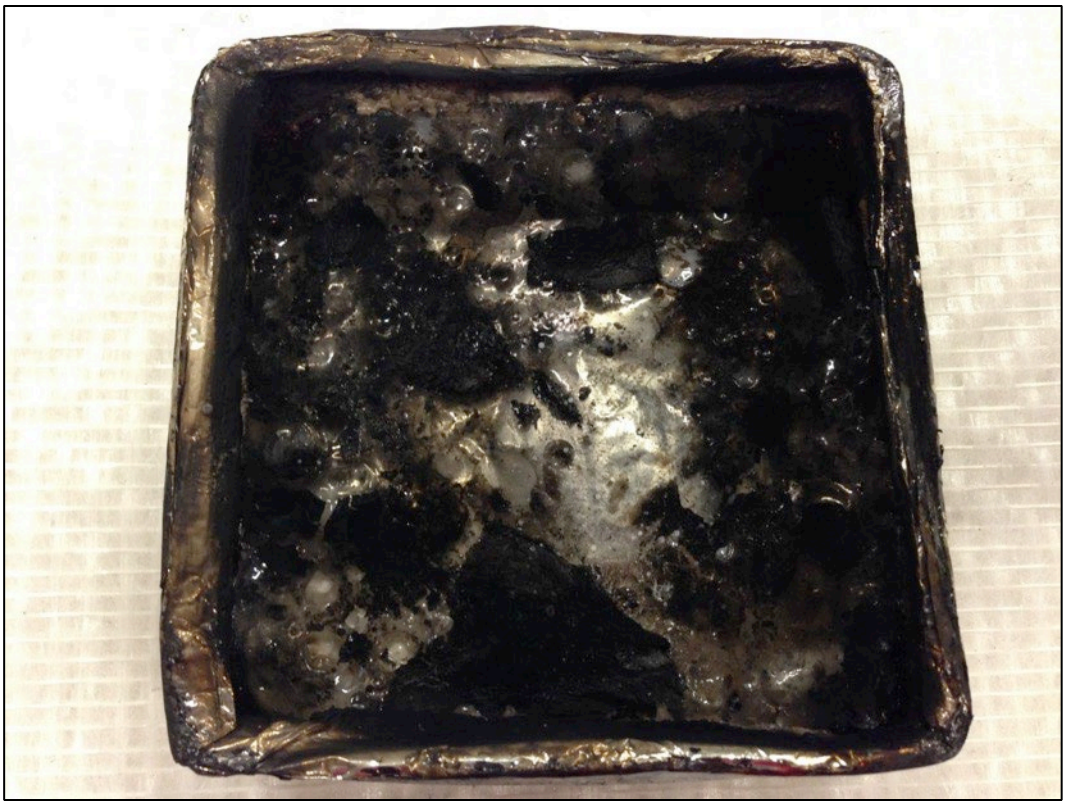
Table 3

Irradiance [kW/m2]	Mass loss rate [g/m^2•s]
30	11,8
40	14,9
50	17,4

Residue examination

After the borated polyethylene had been combusted there was a colourless glass-like residue left with some tar in the aluminum foil wrapping. The residue is presented in Figure 2.

Figure 2: Colourless glass-like residue after combusting borated polyethylene.



The average weight of the residue could be determined to 50,6 g. By dividing the residue weight by the sample weight of 298 g the average residue part was determined to 17 %. It is likely to believe that the residue contains the Boron oxide additive as the supplier stated its content to be 16 %.

Conetools

Obtained values from cone calorimeter tests were imported into Conetools to determine parameters as FIGRA(Fire Growth Rate), Total Heat Release, Euroclass and Time to Flashover. According to the Conetools manual [4] the values obtained at an irradiance of 50 kW/m^2 should be used as design values by preference. As the tests were performed at varying irradiance levels, each level was used as input, which is according to the software also possible as the program has a procedure to adapt results from other irradiance levels.

FIGRA by SBI

The FIGRA parameters are presented in Table 4 as calculated max-values in total and at energy thresholds at 0,2 MJ and 0,4 MJ. The value at each irradiance level is initially based as an average of 3 repeated tests.

Table 4

Irradiance [kW/m^2]	$FIGRA_{max}$ [W/s]	$FIGRA_{02max}$ [W/s]	$FIGRA_{04max}$ [W/s]
30	203,5	203,5	203,5
40	355,5	355,5	355,5
50	470,9	470,9	470,9

In Table 5, the FIGRA parameters with energy thresholds are presented in a sensitivity analysis when the time to ignition, t_{ign}, differs by 10 %. The value at each irradiance level is initially based as an average of 3 repeated tests.

Table 5

Irradiance [kW/m²]	$FIGRA_{02max}$ (t_{ign}+10%) [s]	$FIGRA_{02max}$ (t_{ign}-10%) [s]	$FIGRA_{04max}$ (t_{ign}+10%) [s]	$FIGRA_{04max}$ (t_{ign}-10%) [s]
30	198,0	208,7	198,0	208,7
40	347,8	367,7	343,9	367,7
50	460,1	488,1	454,6	488,1

Total Heat Release at 600 seconds, THR_{600s}, by SBI

The THR_{600s} parameter is presented in Table 6 as calculated values as well as in a sensitivity analysis. The value at each irradiance level is initially based on an average of 3 repeated tests.

Table 6

Irradiance	THR600s [MJ]	THR600s(t_{ign} + 10%) [MJ]	THR600s(t_{ign} - 10%) [MJ]
30	19,9	19,6	20,3
40	43,1	41,2	45,2
50	64,3	61,5	67,3

Euroclass

All calculations in Conetools at the 3 irradiance levels present borated polyethylene as a **D**-classified material according to European fire classification of materials, construction products and building elements. The classification is valid when the material is used as roofs or wall linings, not floorings.

Time To Flashover, TTFo, by RCT

The TTFo parameter is presented in Table 7 as calculated values as well as with a sensitivity analysis. The value at each irradiance level is initially based on an average of 3 repeated tests.
Materials should by preference be tested at 50 kW/m^2 and the results from lower irradiance levels can be seen as an additional sensitivity analysis.

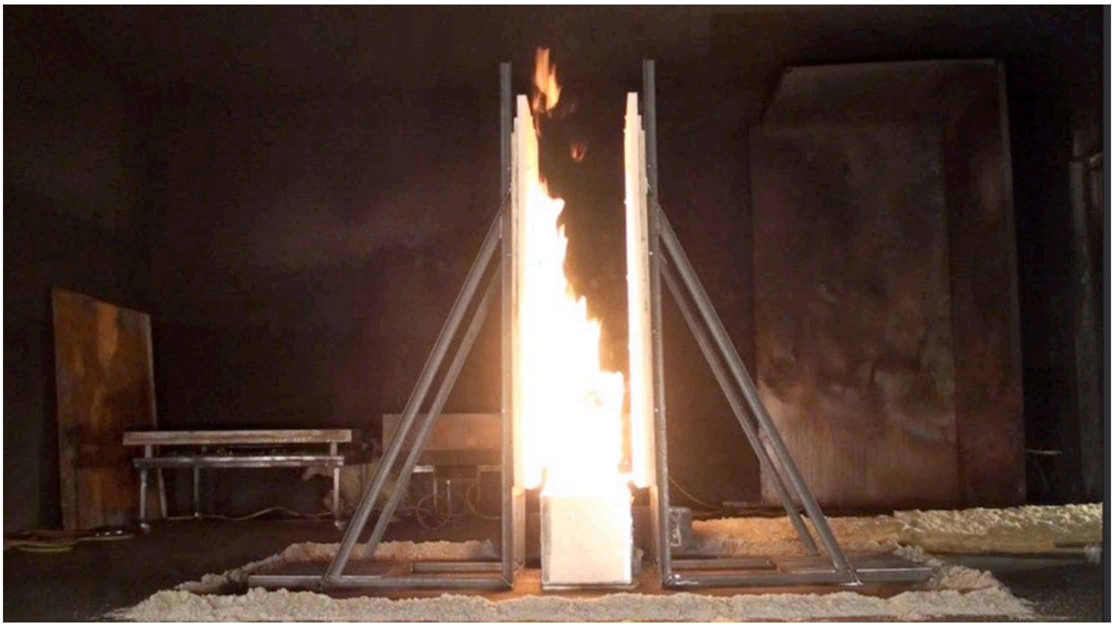
Table 7

Irradiance [kW/m²]	TTFo[s]	TTFo(t_{ign} + 10%) [s]	TTFo(t_{ign} - 10%) [s]
30	462	448,7	477,7
40	385,3	387,7	385
50	344,3	351,3	339

Parallel Panel test

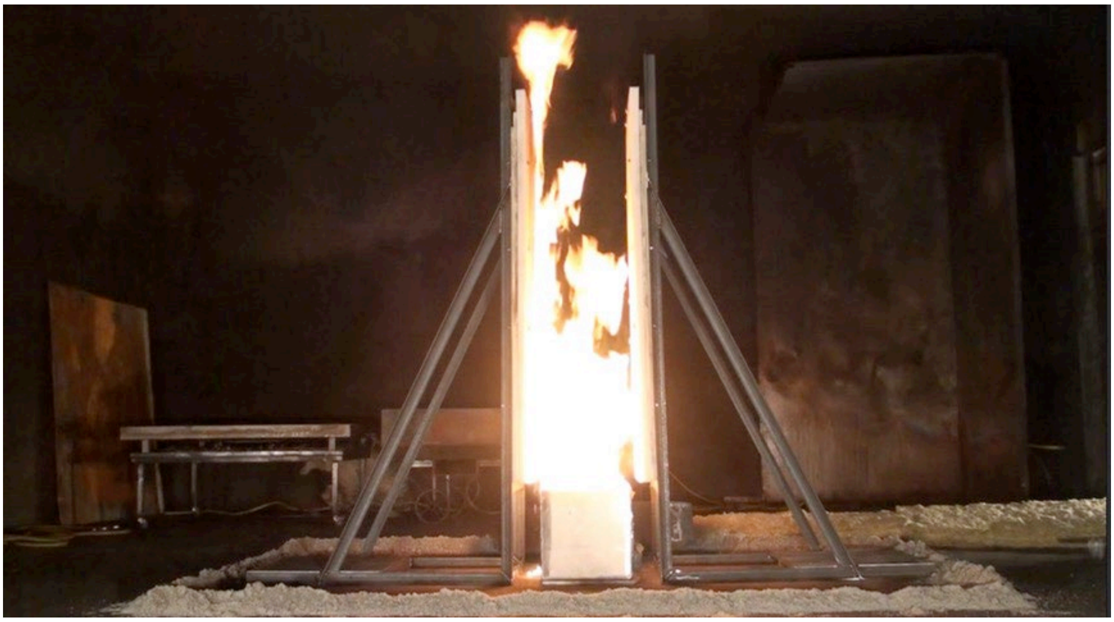
From the parallel panel test, quantitative and qualitative results were obtained. The parallel panel test was set-up with inspiration from the test developed by FM but due to size limitation some adaption needed to be done [3].
When the sand burner was lit it showed that the ventilation caused the flame to bend over nearer to the left sample sheet and after a small adjustment of lowered ventilation flow the flame went more upright but still as shown in Figure 3.

Figure 3: The sand burner is lit.



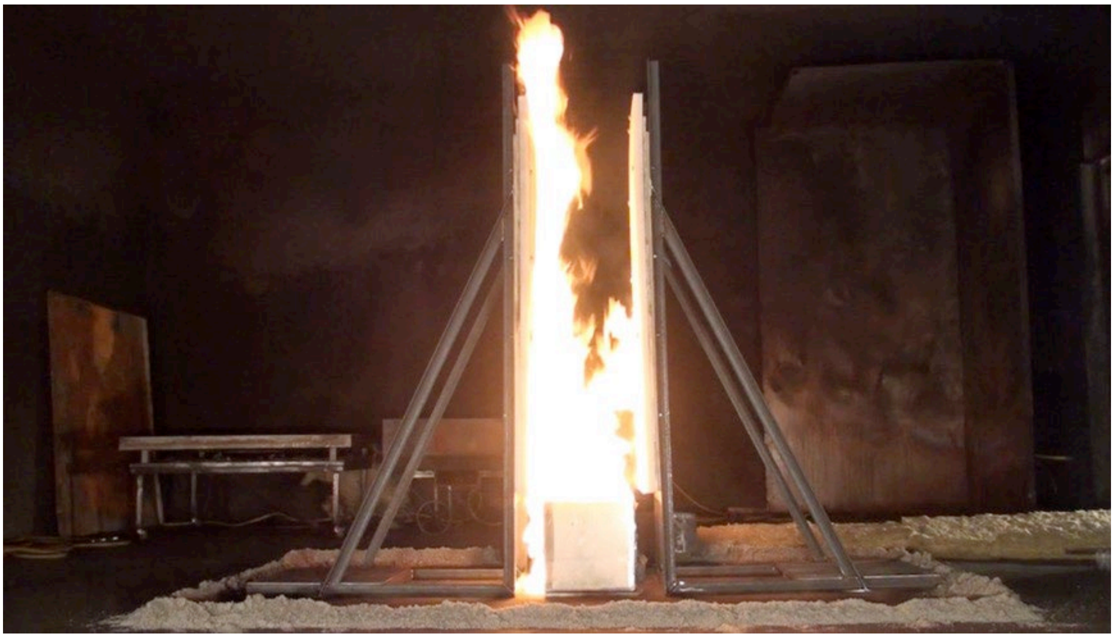
After 2:10 (minutes:seconds), the left material plate started dripping melted material that was burning and 5 seconds later the lower part of the material plate was ignited, see Figure 4. The left material plate had major dripping after 2:30.

Figure 4: The left material plate is ignited and some burning material drops on the floor.



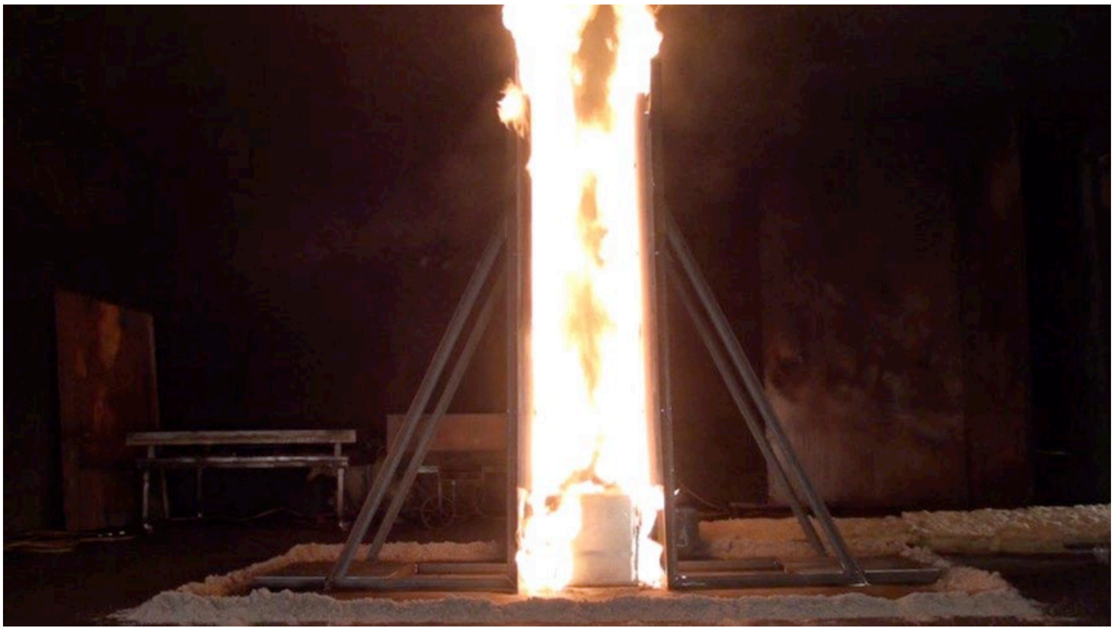
After 4 minutes the right sample sheet started to burn as seen in Figure 5 .

Figure 5: Both material plates are burning



The fire propagation was quite high and as the maximum heat release at the fire lab is 1 MW the propane flow was shut off after 4.50. In Figure 6 it is shown that the sand burner is not delivering any heat to the fire after which the propane gas flow was shut off.

Figure 6: Propane gas flow is shut off (no flames at the sand burner's top).



At 5 minutes, the total area of both samples was engaged in the fire. Figure 7 shows the burning sample sheets with a burning melted material beneath the sample sheets at 8:20. The fire had then been burning for 3:30 after the propane gas flow was shut off. The fire propagated until the fire was extinguished at 10 minutes.

Figure 7: The whole area of the material plates is burning together with the melted material on the floor.

The first fire sequence was nearly extinguished when shutting off the sprinkler system. Small flames on the sample sheet and flaming melted material were left of the fire, as shown in Figure 8.

Figure 8: Small flames left after extinguish attempt.

The remaining fire after the first extinguishment attempt propagated without any help from external heating to a fully developed fire with the total sample area engaged within 11 minutes.

Whole area of the 2 sample plates is burning again as shown in Figure 9.

Figure 9: Both sample areas are engaged in the fire.

After the last extinguishment of the fire with the water sprinkler system it can be seen in Figure 10 that the lower parts of the material plates are heavily damaged by heat and fire. Below the material plates, the melted material has piled up. The melted material contained a lot of hard granular residues likely to be boron oxide. Notable is that the melted material did not cause a pool fire but seemed to be solidified as it got in contact with the gypsum plasterboard.

Figure 10: The melted material is piled up beneath the material plates.

Smoke potential

Table 8 presents the results of the tests made to determine the smoke potential. The conditions during the tests were that material was burning with flames at a mass loss rate of 1-4 g/10s.

Table 8

Test	Smoke potential [Obscura•m³/g]
1	0,40
2	0,21
3	0,52

CONCLUSIONS

The work has resulted in information that is concluded and summarized in this paragraph.

Borated polyethylene

The borated polyethylene is a polyethylene-based material with a 16 % content of Boron oxide, the pure Boron content is 5%.

The Boron oxide additive does not burn or vaporize at temperatures and conditions related to the tests in this report instead it remains as a residue after the test sample has been combusted in the cone calorimeter tests. Earlier studies [1] have shown that the borated material has flame retardant properties in relation to the base polyethylene when combusting the material in a horizontal orientation in a cone calorimeter test. In this horizontal cone calorimeter test, the borated material also self-extinguished when the cone heater is shut off while the base polyethylene continues burning without an influent radiation. The self-extinguishing properties is probably due to several causes as the higher density of Boron and the lower amount of polyethylene but the most significant cause is the residue of Boron oxide that accumulates as a suffocating layer. Still this material is being classified in Euroclass D as a material that are limited in use depending on actual building class of the building due to a simplified design according to the Swedish National Board of Housing, Building and Planning, BOVERKET. This is in the aspect as the borated polyethylene sheets are used without any fire protection measures or extended fire protection system.

In the parallel panel test, where the material plates 0,68 x 1,3 m were burning vertically, it was obvious that the material had less flame retardant properties than in the horizontally burning cone calorimeter test. Once the material was ignited by the sand burner at 60 kW (size of a burning waste basket), it propagated to engage the total sample area within 5 minutes. The burning material also had major dripping of burning melted material. This burning melted material continued to burn on floor and contributed to overall heat release. These burning droplets have a major impact on the use of the material as it is mostly prohibited to use material unprotected with this property. The initial phase of fire propagation was confirmed after the first extinguishing attempt. Small flames remained at the material that then developed again to a new fully developed fire without any external heat flux within 11 minutes after extinguishment. The less flame retardant properties can be derived to that when burning in vertical orientation, the Boron oxide leaves with the melted material and does not interfere the burning process as it does when creating a suffocating layer as the material burns in a horizontal orientation.

Building codes and classification

The Euroclass D classification of borated polyethylene as well as the experienced fire propagation and burning droplets from the parallel panel test makes the material difficult to use without fire protection measures.

BFS 2013:11 BBRBE 1, 3.4 Skyddad brandenergi

The general advice puts a larger responsibility on the owner regarding the verification of fire protection measures. Fire protection measures should be verified by relevant literature or experiments.

FUTURE WORK

To ensure a safe building and environment when using combustible shielding materials it is of the greatest interest to verify all fire protection measures to a reasonable safety level. To do this following work is suggested.

Borated polyethylene

Verification of fire protection measures as linings or other applications.

Borated paraffin

The application of blockhouse wax walls should be verified both theoretically and as a relevant test. Questions such as, depending on the design fire scenario, will the encapsulated paraffin reach the boiling point of water? Will the water content of the Boric acid vaporize? Will the blockhouse wax wall be pressurized and to what degree and what measures can be taken? Will it be necessary to make and verify fire protection measures on the blockhouse wax walls as well?

New materials

Discussions have been made with suppliers regarding developing a new specific fire retardant material for radiation shielding. It would have been desirable to have a shielding material that can be used without thinking of fire protection measures.

REFERENCES

[1] D. Madsen, "Department of Fire properties of borated paraffin and borated polyethylene," 2013.

[2] ISO, "ISO 5660-1:2002," the International Organization for Standardization, 2002. [Online]. Available: http://www.iso.org/iso/home/store/catalogue_tc/catalogue_detail.htm?csnumber=35351.

[3] FM Global, 2013. [Online]. Available: http://www.fmglobal.com/assets/pdf/fmapprovals/4910ansi1.pdf. [Accessed 12 11 2013].

[4] P. van_Hees, A. Steen_Hansen and T. Hertzberg , "Development of a Screening Method for the SBI and Room Corner using the Cone Calorimeter Nordtest project 1479-00," SP Sveriges Provningsinstitut & SINTEF, 2002.

[5] ESS AB_1, 2013. [Online]. Available: http://europeanspallationsource.se/european-spallation-source-0. [Accessed 12 08 2013].

[6] ESS AB_2, 2013. [Online]. Available: http://europeanspallationsource.se/ess-story. [Accessed 12 08 2013].

[7] SFPE, Handbook of fire protection engineering, Third ed., 2002.

[8] Boren, NATIONAL BORON RESEARCH INSTITUTE, 27 06 2013. [Online]. Available: http://www.boren.gov.tr/en/icerik.php?id=27. [Accessed 27 06 2013].

[9] P. Atkins and L. Jones, Chemical principles, FIfth ed., W.H. Freeman and Company, 2010, p. 630.

[10] SP, Sveriges Tekniska Forskningsinstitut,, 2013. [Online]. Available: http://www.sp.se/en/index/information/fireclassification/sidor/default.aspx. [Accessed 12 11 2013].

[11] Boverket_1, "Boverket," 2013. [Online]. Available: http://www.boverket.se/Global/Webbokhandel/Dokument/2012/BBR-engelsk/BFS%202011-26%20Avsnitt%205.pdf. [Accessed 29 11 2013].

[12] BFS 2013:11, "Boverket," [Online]. Available: http://www.boverket.se/sv/lag--ratt/forfattningssamling/gallande/bbrbe---bfs-201311/.

[13] M. L. Janssens, "Analysis of cone calorimeter ignition data: A reappraisal," San Antonio, 2013.

[14] J. Donald Hopkins, "Predicting the ignition time and burning rate of thermoplastics in the cone calorimeter," 1995.