

EXTERNAL LAB REPORT
SUSTAINABLE BINDERS
FOR REFRACTORIES



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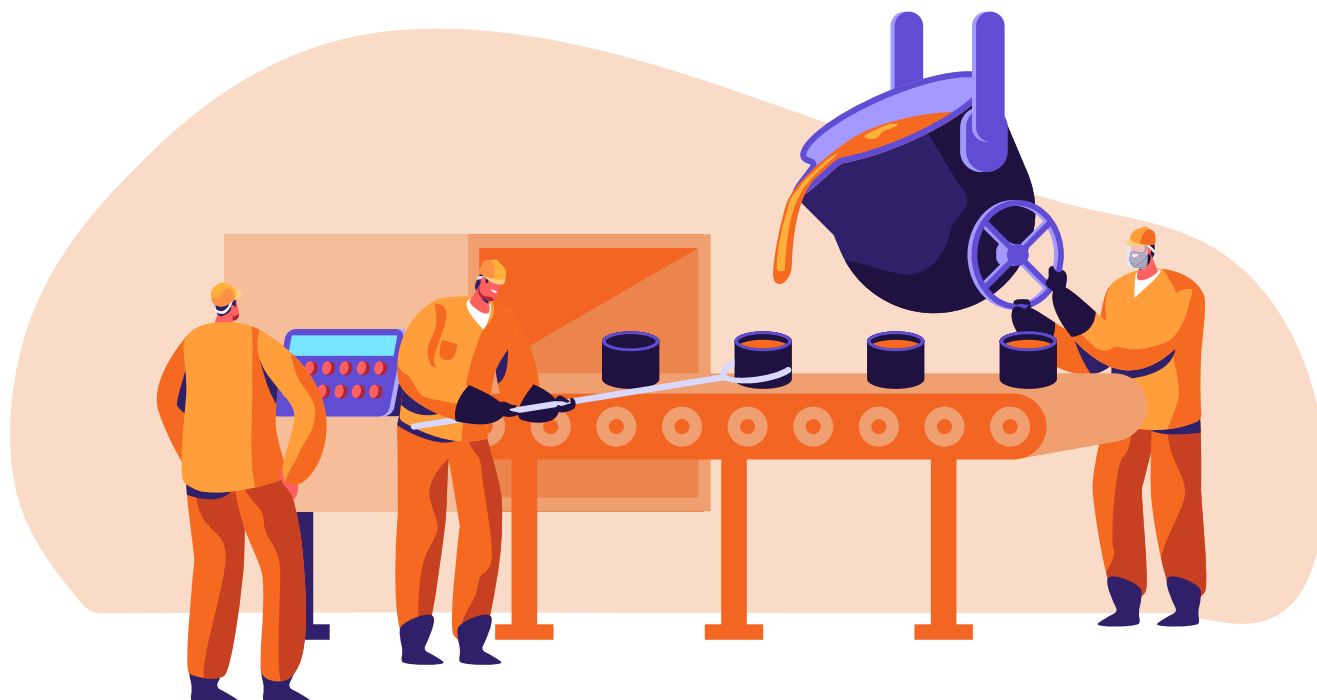


INTRODUCTION

Lignin-based biopolymers are a heterogeneous amorphous organic polymer. They are surface active and contain a large variety of functional chemical groups which makes possible interaction with other substances of different chemical nature. These physico-chemical features of biopolymers are modified undergoing different treatments to optimize their performance. Therefore, their chemical formula and, thus their properties, differ substantially within our range of products.

Biopolymers are largely used as temporary organic additives in the refractory industry not only as binders, but also as plasticisers, lubricant, retardants, etc. The most suitable additive highly depends on the type of refractory and the requirements of each customer. Consequently, the technical support team from Borregaard can recommend the best product for our customers' needs.

Here we explore the advantages of using Borregaard's biopolymers both for shaped refractories – binders and lubricants – and for monolithics.



BINDERS IN SHAPED REFRACTORIES

Our products are highly effective temporary organic binders in both shaped and monolithic refractories. Lignin-based biopolymers act as binders due to their active and strong interactions formed between the different functional groups of the biopolymers and the charged surface of the refractory particles.

All our products have shown an increase on the green and, particularly on the dry strength of the refractory articles. Moreover, they also act as lubricant, enhancing the compaction of the material during pressing resulting in more dense articles.

We have run tests at an external technical institute, IDONIAL, in Spain, where we prove that our biopolymers outperform sugar-based binders.

The material selected in this case was a magnesia with a specific surface of 0.46 m²/g and the following chemical composition:

Table 1: Chemical composition of magnesia used for the tests.

	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O
Average	<0.1	<0.1	0.26	<0.1	2.04	97.06	<0.03	<0.1
U	-	-	0.05	-	0.07	0.42	-	-

The particle size distribution was:

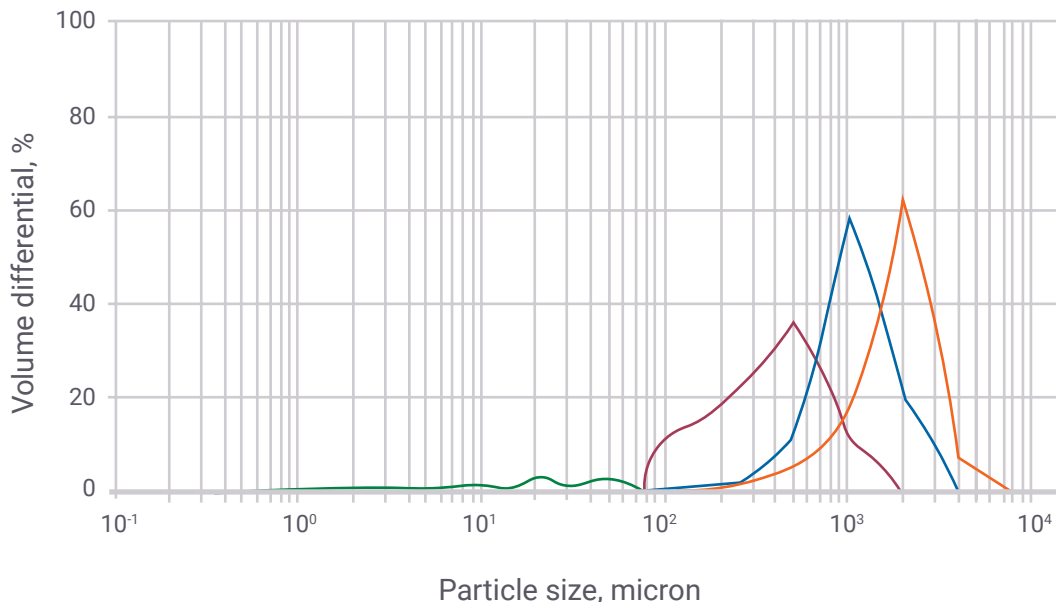


Figure 1: particle size distribution of the magnesia used in the tests.

We tested the apparent density (AP), the cold crushing strength (CCS) and the module of rupture (MOR).

BRICK DENSITY

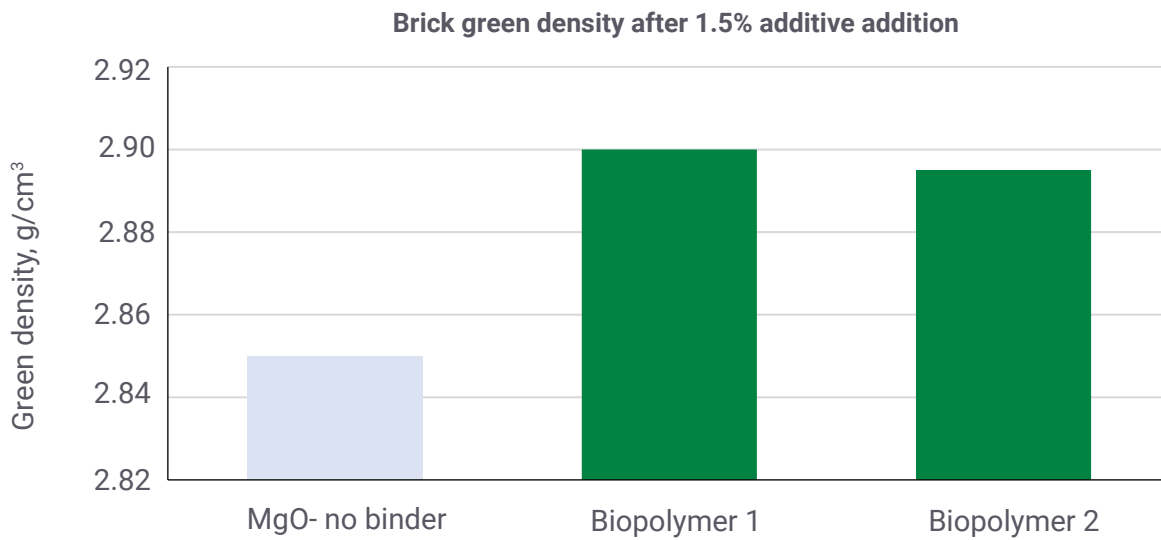


Figure 2: Green density of a magnesia brick without additive and with 1.5% of 2 biopolymers

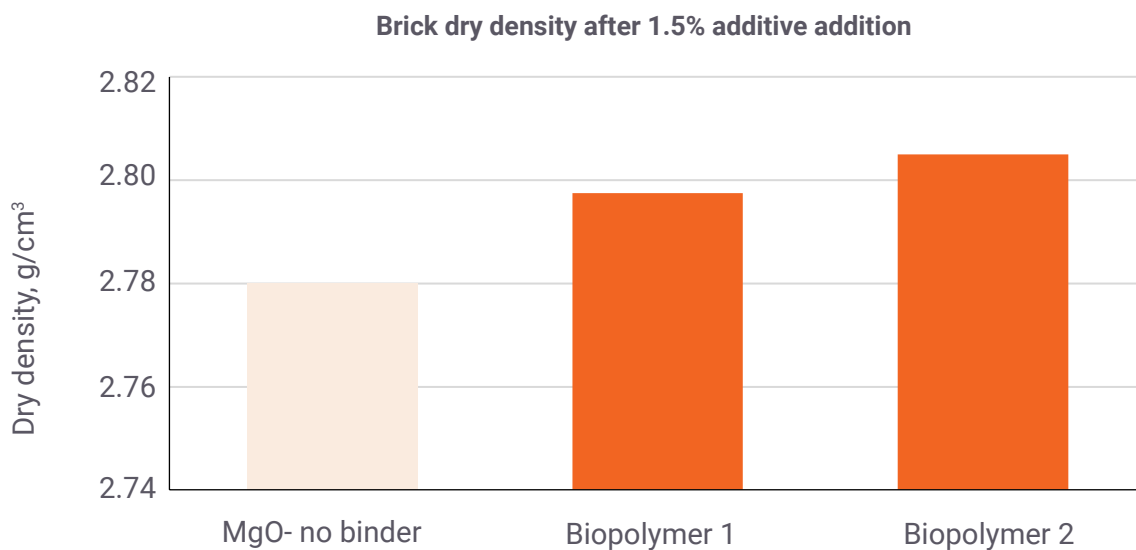


Figure 3: Dry density of a magnesia brick without additive and with 1.5% of 2 biopolymers.

GREEN STRENGTH – COLD CRUSHING STRENGTH & MOR

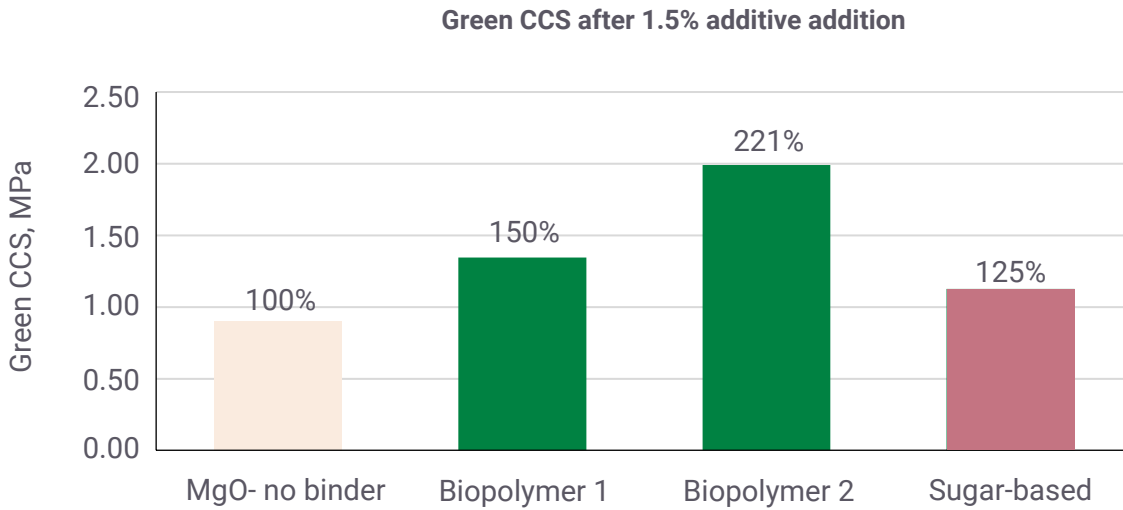


Figure 4: Green CCS of a magnesia brick without additive and with 1.5% of 2 biopolymers and a sugar-based additive.

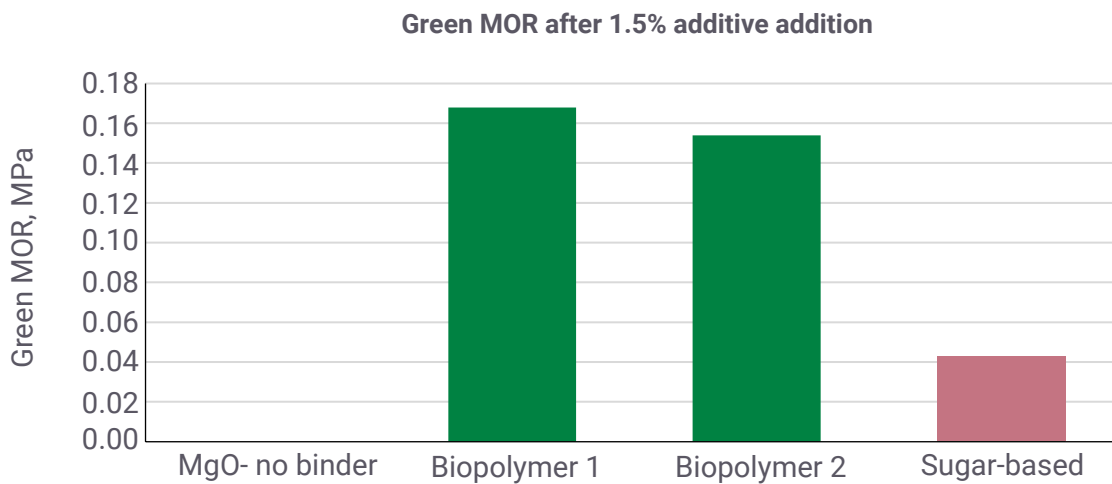


Figure 5: Green MOR of a magnesia brick without additive and with 1.5% of 2 biopolymers and a sugar-based additive.

DRY STRENGTH – CCS & MOR

Our biopolymers are outstanding binders in dry bricks showing a dramatic increase in both dry CCS and MOR. This increase in strength provided by our products helps to reduce handling losses during both the drying and firing stages of production.

As can be seen from the graphs below the dry CCS values increase between 5 to 9 times whilst the dry MOR increases between 2 to 4 times the value of the reference without binders.

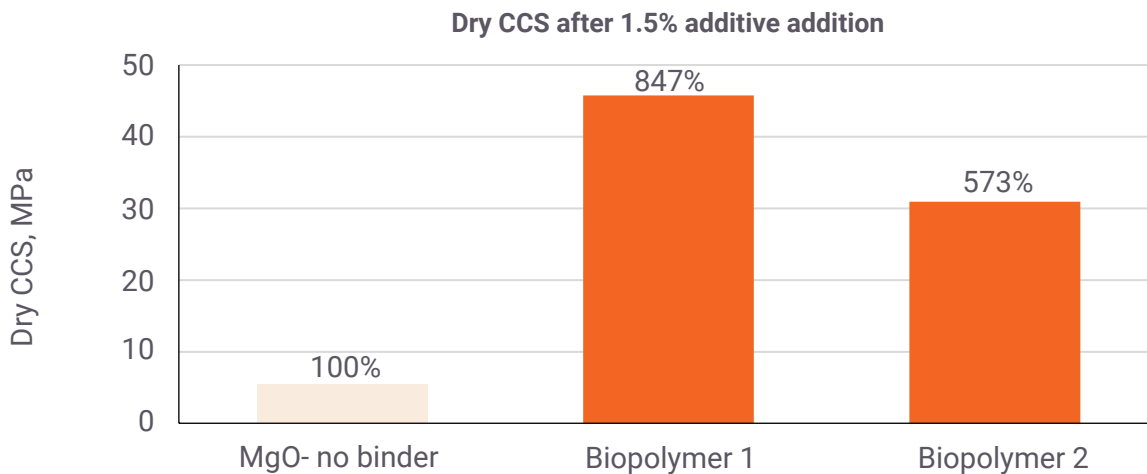


Figure 6: Dry CCS of a magnesia brick without additive and with 1.5% of 2 biopolymers.

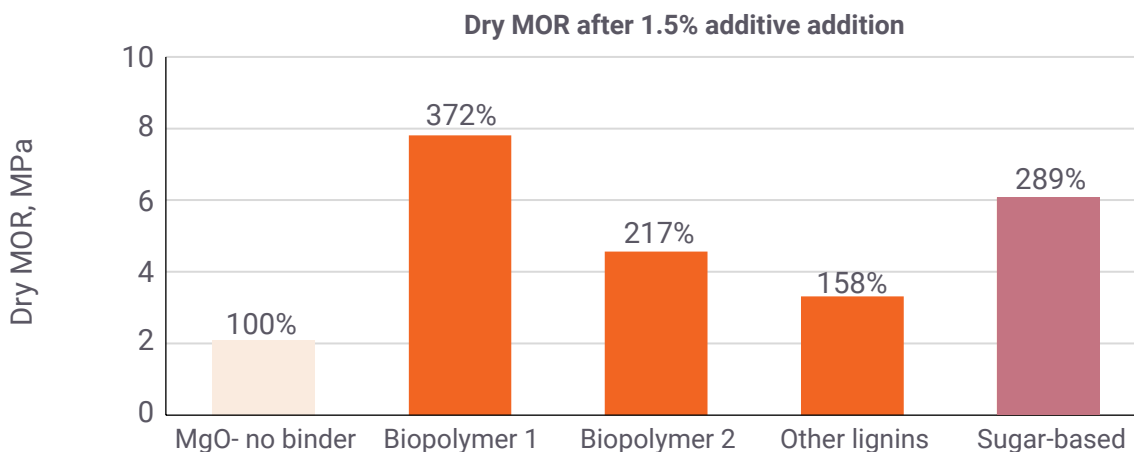


Figure 7: Dry MOR of a magnesia brick without additive and with 1.5% of 2 biopolymers, another lignin-based additive and a sugar-based additive.

DRYING

MAGNESIA AGEING

It is known that under certain production conditions, the quality of the magnesia decreases when it is mixed with liquid additives and left for a period of time before pressing the brick. This effect is more pronounced at temperatures above room temperature, i.e. 50 °C.

Some additives are particularly sensitive to ageing decreasing both density and dry strength of the pressed bricks. Borregaard have designed products with low sensitivity to ageing, giving superior performance against alternate products when manufacturers need to leave the mix for a period of time. As shown in the graph below Borregaard biopolymers outperform both alternate lignin's and sugar-based additives.

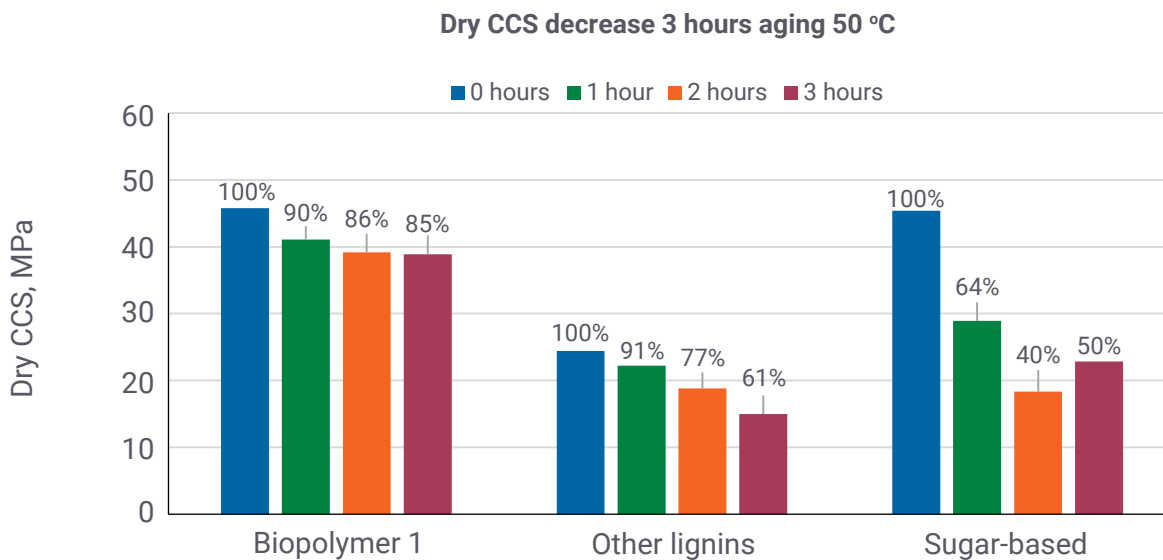


Figure 8: Decrease in CCS after addition of a Borregaard biopolymer, other lignin-based additives and a sugar-based additive.

BIOPOLYMERS FOR MONOLITHIC REFRACTORIES

INCREASED GREEN AND DRIED BODY STRENGTH

Borregaard has specifically designed several plasticizers, retardants, dispersants and binding products for monolithic (unshaped) refractories.

Our range of products are used in monolithics to increase the mechanical resistance, bringing very good properties as temporary binders with dosages between 0.5 to 7%.

The main (monolithic) application where our products are well established is in mortar production, where our biopolymers work as both binder and plasticizer, without compromising fluidity, replacing other unsustainable alternatives like synthetic polymers.

One of the challenges in formulating monolithic refractories is to achieve the right rheological and dispersion properties with a low water content. For example, many castable materials with a low cement content require the use of a deflocculant or dispersant to give high flow at a low water content. Borregaard's special range of products offer high dispersant properties with dosages as low as 0.01-0.5%. These products are very effective in formulations where hydrophobic materials like carbon or thermal black are introduced into the refractory aggregate.

USE OF HIGHLY MODIFIED PRODUCTS FOR CARBON BLACK DISPERSION IN REFRACTORARY MIXES

Tailor-made biopolymers are amongst the most effective carbon black dispersants available on the market today [2]. They are the preferred dispersants to ensure uniform mixing of carbon black and pitch binder (both hydrophobic) in refractory mixes, e.g., water-based alumina refractory for making linings via casting or spraying.

Carbon black is used as an alternative to micro silica in alumina aggregates. The addition of carbon black entails a challenge in ensuring uniform mixing and dispersion of the ultrafines because carbon black is chemically different (i.e., more hydrophobic) than micro silica. Other dispersant additives available in the market for monolithic alumina castables might be sodium hexametaphosphate (Na-HMP) or sodium tripolyphosphate (STP). However, Na-HMP and STP do not adequately disperse hydrophobic carbonaceous material such as carbon black. This requires the use of a specific dispersant to ensure uniform mixing of the carbon black or pitch throughout the matrix. Our additives ensure uniform mixing of minority hydrophobic components in a wet matrix. Next figure, extracted of a patent (US 6,313,055 B1), shows that Marasperse CBA-1 is a better dispersant than STP and naphthalene sulfonate in high alumina with ultra-low cement content using thermal black. [3]

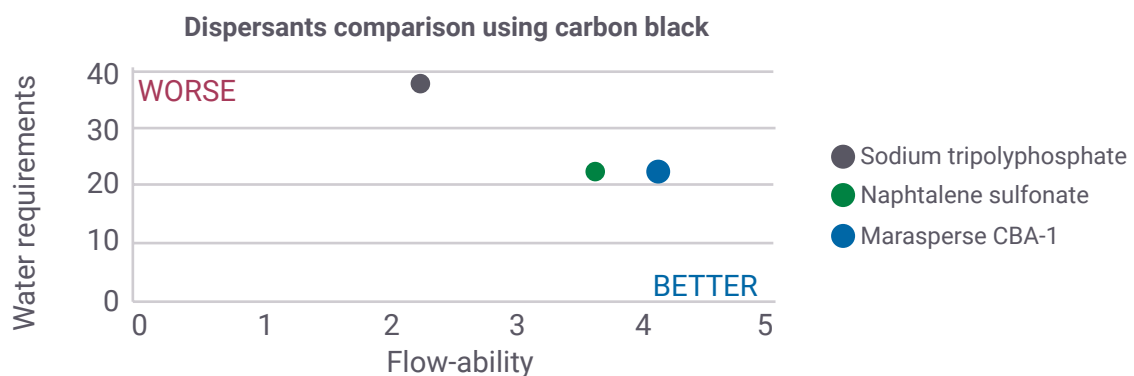


Figure 9: Comparison of performance of Marasperse CBA-1 vs Na-HMP and STP.

USE OF DISPERSANT ADDITIVES IN GENERAL REFRACTORY MASSES

For general refractory masses, there is a range of products available offering high, intermediate and basic dispersion performance. These have been seen to be useful in monolithic refractory castables, especially in masses with medium (MCC), low (LCC), ultra-low (ULCC) and no cement content (NCC), where there is a need for the use of ultrafine particles and a dispersant agent, with a recommended dosage between 0.01 and 0.5%.



REFERENCES

1. Nodosvitii, V.P., et al., Use of lignosulfonates as binders in refractories. *Refractories*, 1994. 35(5): p. 145-150.
2. Pattillo, R.A. and S.B. Bonsall. Cement-free refractory. US20120142518A1. Vesuvius USA Corp, 2012.
3. Cullen, R.M. Refractpru Castables Containing Thermal Black. US 6,313,055 B1. Harbison-Waker Refractories Company, 2001.



ABOUT US

Borregaard operates the world's most advanced and sustainable biorefinery. By using natural, sustainable raw materials, Borregaard produce advanced and environmentally friendly biochemicals and biomaterials that replace oil-based products. Our world-wide network of production facilities and sales offices assures the very best local service and competence where you need it. For us, providing our customers with the most dedicated technical assistance is key. Therefore, the company invests considerable resources in research and development. We continuously strive to develop wood based renewable products for new applications, and through that we contribute to delivering present alternatives to oil based synthetic products in a wide variety of industries.

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