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MgO-C LADLE BRICKS BASED ON RECYCLATES AND A LIGNIN-COLLAGEN-FRUCTOSE BINDER SYSTEM

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ABSTRACT

Every year, approx. 28 million tons of used refractories accrue worldwide. After their break out, the majority of them are used in subordinate application fields such as aggregates for road construction (downcycling) or deposited in landfills. Their recycling in the field of refractory materials played an underpart so far. For ecological and economic reasons, an increased research potential was identified in the last years consecrated to increasing the recycling rate of refractories and finding new markets and application fields with higher value for them. The study presents current findings of a long-term research training group addressing (amongst others) the development of MgO-C ladle bricks containing MgO-C recyclates and being bonded with pitch- and resin-free environmentally friendly binders. So far, the favored batches contained an oxidic grain fraction composed of 40.5 wt.-% fused MgO raw material, 40.5 wt.-% MgO-C recyclates, 14 wt.-% sintered magnesia (DBM) raw material together with 5 wt.-% graphite and optional antioxidants (TiO_2, Al, SiO_2). A binder system composed of a mixture of lignin, collagen, and polyethylene glycol (PEG) was developed. The latter served as a pressing aid and was necessary due to the absence of liquid resin in the batch. Even after a considerable and auspicious optimization during previous studies, this basic batch containing recyclates and no pitch or resin does not meet the physical and mechanical properties of standard industrial bricks. Hence, in the present study, the binder system was enhanced by using varying amounts of lignin, collagen, and tannin together with polyethylene glycol, fructose, and citric acid addition. The new developed MgO-C mixtures were pressed uniaxially, dried, cured, and carbonized at 1000 °C. It has been found that polyethylene glycol, which impairs the material properties, can be omitted using sufficient amounts of fructose. The addition of citric acid leads to a further increase in CCS. Consequently, actual optimized environmentally friendly MgO-C batches show a CCS of 85 % of the value of industrial pitch- and resin-bonded bricks without recyclates.

INTRODUCTION

Refractory materials are used in high-temperature applications where they are e.g. in contact with molten metal and slag. Therefore, they require particular properties such as high thermal shock resistance, corrosion and erosion resistance, and sufficient mechanical strength at room and elevated temperatures[1]. Magnesia-carbon (MgO-C) bricks were initially developed for electric furnaces in the 1970s and later adopted as working linings for converters (BOF) and secondary refining processes (ladle). In general, MgO-C bricks contain a carbon (graphite) content of up to 30 wt.-% and are bonded by phenolic resin or pitch[2]. Graphite plays a crucial role in inhibiting steel and slag penetration into the brick structure due to its low wettability by molten slag. Moreover, the addition of graphite significantly enhances the thermal shock resistance compared to carbon-free sintered magnesia due to its high thermal conductivity and low coefficient of thermal expansion[3].

It is well known that the choice of binder is essential for all refractory ceramics. However, a binder that is suitable for carbon-containing refractories has to meet further specific. Therefore, a large variety of organic binders has been tested for carbon-containing refractories. Apart from a few special applications, pitches and phenol formaldehyde resins nowadays dominate the market in the bonding of carbon-bonded products[4]. Their pyrolysis (carbonization) delivers a three-dimensional cross-linked lattice, which is very hard, insoluble, and stable. However, phenol-formaldehyde resins and pitches are highly harmful to human health and environment. Formaldehyde has carcinogenic as well as suppressive effects on the nervous system of animate beings. Phenol formaldehyde resins have harmful effects on the skin, causing dermatitis and eczema[5]. Additionally, the pyrolysis of coal tar pitches results in the release of hazardous compounds such as benzo[a]pyrene. Such compounds are harmful even at low concentrations because of their bioaccumulation properties. Therefore, the European Chemicals Agency imposes in their REACH regulation strict protocols for transporting and processing all polycyclic aromatic hydrocarbons (PAHs).

Consequently, research activities were undertaken to reduce the toxicity of binders while maintaining the relevant properties of the components. Zhao et al. developed graphite electrodes bonded by biomass and its derivatives that can offer sustainable alternatives to petroleum-based materials[6]. In particular, sustainable alternative binders need to exhibit a high coke yield, cross-linking of PAHs, and a high atomic C/H ratio.

Lignin is the second most abundant aromatic polymer and has been traditionally relegated to be used as a low-grade fuel. During the pyrolysis, lignin undergoes a free radical chain-reaction mechanism similar to the liquid-phase carbonization of coal tar pitch. Free radical precursors that are generated during the heat treatment undergo cross-linking, aromatization, and rearrangement reactions leading to the formation of highly condensed aromatic rings and consequently heterogeneous carbon structures of graphitic nature. Hence, high-purity lignin represents a candidate for the manufacturing of high-temperature binders and carbonized materials due to its appropriate structure and behavior[7].

Collagen is derived from the hides and residues from the meat-packing industry. Owing to its ampholytic character with ionizable groups and active sites for cross-linking reactions, collagen acts as a strong binder. Early studies revealed that it can be used in combination with other additives as a core binder for iron casting in foundries[8]. It also releases a lower amount of volatile organic compounds, hazardous air pollutants, and greenhouse gas emissions compared to conventional phenolic-based binders.

In this study, MgO-C bricks were developed utilizing spent refractories (MgO-C recyclates) to contribute to lower CO_2 emissions during fabrication compared to the use of MgO originating from $MgCO_3$ raw material. In addition, the combination of lignin, tannin, and collagen as environmentally friendly binders for MgO-C ladle bricks containing a high amount of MgO-C recyclates was employed and investigated. Furthermore, the impact of polyethylene glycol (PEG), fructose, and citric acid on the processing and the material properties of the environmentally friendly MgO-C bricks was explored.

MATERIALS AND METHODS

Materials

The raw materials used for processing MgO-C samples include both fused MgO and recycled MgO-C. The fused MgO (97.5 % purity, Refratechnik Steel, Germany) was utilized in the grain size fractions 3-7 mm, 1-3 mm, and 0-1 mm. The MgO-C recyclates (Refratechnik Steel, Germany) were obtained in the grain size fractions 3-6 mm, 1-3 mm, and 0-1 mm. In comparison to the fused MgO raw material, the recycled MgO-C materials exhibit a varying content of residual carbon that remains in conjunction with the MgO grains after breakout and processing as well as other impurities that were picked up during the first application as lining

material for the continuous casting process. The amount of residual carbon and the impurities was found to depend on the size fraction of the recyclates. Next to coarse fused MgO and MgO-C recyclates, fine sintered magnesia (DBM, purity > 97 %, both Refratechnik Steel, Germany) was added with particle sizes below 45 µm. The MgO-based general composition that was kept constant for all batch variations is presented in Tab. I.

Tab. I: MgO-based composition (wt.-%) of the batches with (50R) and without MgO-C recyclates (FM).

Raw material	*Batch FM*	*Batch 50R*
Fused MgO (3-7 mm)	20.7	10.8
Fused MgO (1-3 mm)	33.3	17.3
Fused MgO (0-1 mm)	22.5	11.7
MgO-C recyclate (3-6 mm)	-	10.8
MgO-C recyclate (1-3 mm)	-	17.3
MgO-C recyclate (0-1 mm)	-	11.7
DBM MgO powder	13.5	14.1

Coarse natural flake graphite (NFL 92/94, Graphit Kropfmühl, Germany) served as a carbon source. Alkaline lignin (L0082, TCI, Germany), tannin (quebracho extract, Baeck, Germany), and collagen (100 % pure bovine collagen hydrolysate, FNW International, Germany) were used as binders. Fig. 1 displays the solid binders in their delivery state as powders. Ethylene glycol with a purity of 99 % (Grüssing, Germany) and fructose (Hellmi, Germany) were used to substitute deionized water that served as a pressing aid in previous studies. Fructose is a monosaccharide ($C_6H_{12}O_6$) containing hydroxyl groups. Furthermore, citric acid powder (Carl Roth, Germany) was added as cross-linking agent.

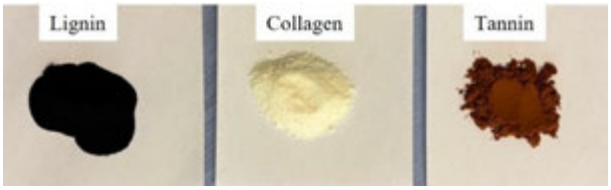

Fig. 1: The solid binders lignin, collagen, and tannin in their delivery state.

Four types of batches with variations in the binder system and pressing aid were designed:
- fructose (F) + lignin (L)/collagen (K) with polyethylene glycol (PEG) (Tab. II),
- fructose (F) + lignin (L)/collagen (K) with citric acid (CA) (Tab. III),
- fructose (F) + collagen (K) with citric acid (CA) (Tab. IV),
- fructose (F) + tannin (T) with citric acid (CA) (Tab. V).

Tab. II: Composition (wt.-%) of the batches containing MgO with fructose (F), lignin (L), collagen (K), and PEG

Raw material	*FM0.6F-2.4L-A-1PEG*	*FM0.6F-2.4K-A-1PEG*
MgO	90.0	90.0
Graphite	10.0	10.0
Fructose	0.6	0.6
Lignin	2.4	-
Collagen	-	2.4
PEG	1.0	1.0

In addition, all batches contain the following additives:
- 2.5 wt.-% Aluminum powder with a purity of ≥ 99 % and a grain size < 160 µm (Carl Roth, Germany),
- 0.5 wt.-% SiO_2 with a purity of 96 ± 1.5 % (RW silicium, Germany) consisting of primary particles (approx. 63 %) with sizes ranging from 0.1 to 0.3 µm along with 1.5 % coarser grains with a maximum size of 45 µm,
- 0.4 wt.-% TiO_2 with a purity > 99 % and a particle size < 45 µm) (Crenox, Germany).

Tab. III: Composition (wt.-%) of the batches containing MgO (FM) and MgO-C recyclates (50R) with fructose (F), lignin (L), collagen (K), and citric acid (CA)

Raw material	*FM2.4F-0.6K-0.3L-A*	*50R2.4F-0.6K-0.3L-A*	*50R2.4F-0.6K-0.3L-A-0.3CA*
MgO	90.0	53.9	53.9
MgO-C recyclate	-	39.8	39.8
Graphite	10.0	6.2	6.2
Fructose	2.4	2.4	2.4
Lignin	0.3	0.3	0.3
Collagen	0.6	0.6	0.6
Citric acid	-	-	0.3

Tab. IV: Composition (wt.-%) of the batches containing MgO (FM) and MgO-C recyclates (50R) with fructose (F), collagen (K), and citric acid (CA)

Raw material	*FM2.4F-0.6K-A*	*50R2.4F-0.6K-A*	*50R2.4F-0.6K-A-0.3CA*
MgO	90.0	53.9	53.9
MgO-C recyclate	-	39.8	39.8
Graphite	10.0	6.2	6.2
Fructose	2.4	2.4	2.4
Collagen	0.6	0.6	0.6
Citric acid	-	-	0.3

Tab. V: Composition (wt.-%) of the batches containing MgO (FM) and MgO-C recyclates (50R) with fructose (F), tannin (T), and citric acid (CA)

Raw material	*FM2.4F-0.6T-A*	*50R2.4F-0.6T-A*	*50R2.4F-0.6T-A-0.3CA*
MgO	90.0	53.9	53.9
MgO-C recyclate	-	39.8	39.8
Graphite	10.0	6.2	6.2
Fructose	2.4	2.4	2.4
Tannin	0.6	0.6	0.6
Citric acid	-	-	0.3

Sample preparation

The raw materials were homogenized for 10 minutes in a mortar mixer (ToniMIX, Toni Baustoffprüfsysteme, Germany) by maintaining a consistent mixing order to ensure reproducibility. The mixing process started with the dry mixing of the coarse grains (3-7 mm and 1-3 mm), followed by the addition of half of the PEG, fructose, or citric acid. In the case of batches containing 2.4 wt.-% fructose, one-half was added, otherwise the full amount of fructose (0.6 wt.-%) was added in this mixing step. Subsequently, the graphite and fine magnesia (0-1 mm) were incorporated into the mixture. In the next step, the binders (lignin, tannin, and collagen) and the additives (Al, TiO_2, and SiO_2) were pre-mixed and added to the mortar mixer. Afterwards, the remaining PEG, fructose (in the case of 2.4 wt.-%), and citric acid were added followed by the finest MgO powder fraction.

Cylindrical samples (50 mm in diameter and 50 mm in height) were pressed with a uniaxial press (ES 270, RUCKS Maschinenbau, Germany) at a maximum pressure of 150 MPa. After pressing, the samples were dried and cured by heating them

with a heating rate of 60 K·h^{-1} to 85 °C and keeping this temperature for 2 h, and a further heating with 55 K·h^{-1} to 220 °C and keeping this temperature for 1 h followed by a free cooling. Afterwards, the samples were embedded in retorts filled with calcined petrol coke (0.2–2 mm, Müco, Germany) and carbonized at 1000 °C applying a heating rate of 100 K·h^{-1}. This temperature was kept for 3 h followed by free cooling.

Methods

After carbonization, the cold crushing strength (CCS) was determined according to the European Standard DIN EN 993-5. The bulk density (BD) and apparent porosity (AP) were determined by toluene immersion according to DIN EN 993-1. Additionally, the permanent change in diameter on heating was detected according to DIN EN 993-10. The mass change during carbonization was determined as well.

RESULTS AND DISCUSSION

Batches containing fructose, lignin, collagen, and PEG

Table VI lists the BD, AP, CCS, permanent change in diameter, and the mass change of the batches composed of fused MgO raw material with fructose, lignin, and collagen as binder system, and PEG as pressing aid (see batch compositions given in Tab. II).

Tab. VI: BD, AP, CCS, permanent change in diameter, and mass change of the batches based on MgO with fructose, lignin, collagen, and PEG (see Tab. II) as well as a resin-bonded reference[9].

	Ref	*FM0.6F-2.4L-A-1PEG*	*FM0.6F-2.4K-A-1PEG*
BD (g·cm^{-3})	2.93	2.71	2.74
AP (%)	10.7	17.8	18.4
CCS (MPa)	30.9	19.1 ± 0.06	19.7 ± 0.67
Permanent change in diameter (%)	-	0.34 ± 0.02	0.19 ± 0.04
Mass change (%)	-	1.08 ± 0.02	1.72 ± 0.11

As already reported by Stadtmüller et al.[9], the replacement of pitch- and resin-binders by 2.4 wt.-% of environmentally friendly binders such as lignin and collagen results in a significantly lower bulk density and a loss of CCS by approx. 40 %. In addition, the AP increases by 70 % from 10.7 % to 18.1 % on average. The comparison of the binders reveals a slight advantage of adding collagen (sample FM0.6F-2.4K-A-1PEG) compared to lignin (sample FM0.6F-2.4L-A-1PEG) regarding the CCS while applying lignin as a binder results in a slightly lower AP. Furthermore, the use of 0.6 wt.-% fructose together with 1 wt.-% PEG showed no significant impact on the AP and CCS compared to samples prepared by using PEG without fructose[9].

The permanent change in diameter during carbonization seems to be sufficiently low to prevent macrostructural damage and crack formation. However, a mass change of at least 1 % compared to the cured state indicates fugitive components, whose amount is higher using collagen.

Batches containing fructose, lignin, collagen, and citric acid

Table VII provides the BD, AP, CCS, permanent change in diameter, and mass change of the batches composed of fused MgO raw material and MgO-C recyclates with lignin and collagen as binder system, fructose as pressing aid, and citric acid as cross-linking agent (the batch compositions are provided in Tab. III).

Even if the samples contain a lower amount of binders, their combination together with a higher amount of fructose and no PEG results in significantly higher CCS and lower AP. This applies to both types of samples containing fused MgO and fused MgO with MgO-C recyclates. However, the already reported negative impact of the recyclates on the properties of the materials compared to recyclate-free batches could be confirmed[9]. Furthermore, the addition of citric acid (0.3 wt.-%) results in a significant increase of CCS and a decrease of the AP of approx. 20 % of the environmentally friendly bonded batches containing MgO-C recyclates, which even exceeds the properties of recyclate-free batches without citric acid usage. The increase in density by using citric acid indicate its positive impact on the pressing.

Tab. VII: : BD, AP, CCS, permanent change in diameter, and mass change of the batches based on MgO (FM) and MgO-C recyclates (50R) with fructose (F), lignin (L), collagen (K), and citric acid (CA) (see Tab. III)

	FM2.4F-0.6K-0.3L-A	*50R2.4F-0.6K-0.3L-A*	*50R2.4F-0.6K-0.3L-A-0.3CA*
BD (g·cm^{-3})	2.79	2.64	2.73
AP (%)	16.3	20.0	15.9
CCS (MPa)	23.3 ± 0.23	21.3 ± 0.97	25.2 ± 0.32
Permanent change in diameter (%)	0.42 ± 0.05	0.47 ± 0.01	0.31 ± 0.02
Mass change (%)	0.96 ± 0.02	0.78 ± 0.07	1.06 ± 0.02

Batches containing fructose, collagen, and citric acid

Table VIII provides the BD, AP, CCS, permanent change in diameter, and the mass change of the batches composed of fused MgO raw material and MgO-C recyclates with collagen as binder, fructose as pressing aid, and citric acid as cross-linking agent (see batch compositions given in Tab. IV).

Tab. VIII: BD, AP, CCS, permanent change in diameter, and mass change of the batches based on MgO (FM) and MgO-C recyclates (50R) with fructose (F), collagen (K), and citric acid (CA) (see Tab. IV)

	FM2.4F-0.6K-A	*50R2.4F-0.6K-A*	*50R2.4F-0.6K-A-0.3CA*
BD (g·cm^{-3})	2.82	2.73	2.73
AP (%)	14.2	18.0	15.9
CCS (MPa)	27.4 ± 1.01	23.6 ± 0.56	26.1 ± 1.03
Permanent change in diameter (%)	0.43 ± 0.06	0.46 ± 0.04	0.36 ± 0.03
Mass change (%)	0.68 ± 0.10	0.71 ± 0.04	0.93 ± 0.05

The high CCS of 27.4 MPa of sample FM2.4F-0.6K-A which is almost 90 % of the CCS of the resin- and pitch-bonded reference proves that MgO-C can be bonded with only 0.6 wt.-% collagen and using a proper amount of fructose (2.4 wt.-% %). The combination of collagen with lignin in a binder system seems not to be necessary. As expected, the AP of the sample FM2.4F-0.6K-A prepared in the laboratory is still significantly higher compared to the reference prepared and pressed applying an optimized manufacturing route in the industry. Additionally, with the absence of lignin, the mass change is also lower indicating a lower amount of fugitive compounds in the batch.

Adding MgO-C recyclates results in an already reported effect of increasing the AP and decreasing the CCS compared to recyclate-free standard batches. However, the positive impact of collagen as a binder without using lignin, and the usage of fructose attenuates the negative effect resulting in higher CCS and lower AP of sample 50R2.4F-0.6K-A compared to 50R2.4F-0.6K-0.3L-A which contains additionally 0.3 wt.-% lignin.

The addition of 0.3 wt.-% citric acid improves the properties also in the samples containing collagen and no lignin resulting in a 10 % higher CCS of sample 50R2.4F-0.6K-A compared to sample 50R2.4F-0.6K-A-0.3CA. Consequently, a CCS of a batch containing MgO-C recyclates and an environmentally friendly

binder could be achieved that is only 5 % lower than a recyclate-free batch and only 15 % lower than a recyclate-free, conventionally bonded batch. However, the mass change increases using citric acid.

Batches containing fructose, tannin, and citric acid

Table IX provides the BD, AP, CCS, permanent change in diameter, and the mass change of the batches composed of fused MgO raw material and MgO-C recyclates with tannin as a binder system, fructose as pressing aid, and citric acid as cross-linking agent (the batch compositions are provided in Tab. V).

Tab. IX: BD, AP, CCS, permanent change in diameter, and mass change of the batches based on MgO (FM) and MgO-C recyclates (50R) with fructose (F), tannin (T), and citric acid (CA)

Raw material	*FM2.4F-0.6T-A*	*50R2.4F-0.6T-A*	*50R2.4F-0.6T-A-0.3CA*
BD ($g \cdot cm^{-3}$)	2.80	2.76	2.73
AP (%)	15.8	15.7	15.0
CCS (MPa)	26.4 ± 0.80	22.5 ± 1.14	25.8 ± 0.76
Permanent change in diameter (%)	0.47 ± 0.04	0.44 ± 0.08	0.38 ± 0.02
Mass change (%)	0.49 ± 0.06	0.52 ± 0.04	0.76 ± 0.03

The effect of tannin binder on the material properties of the MgO-C samples resembles the findings of the previous section reporting on the effect of collagen as a single binder component with fructose addition. The sample 50R2.4F-0.6T-A containing MgO-C recyclates exhibits a lower CCS compared to sample FM50R2.4F-0.6T-A without recyclates. Remarkably, the AP stays on the same level. Adding 0.3 wt.-% citric acid results in an already reported effect of increasing the CCS and decreasing the AP. However, even if the effect of tannin as sole binder on the CCS and AP is superior to the binder system containing lignin and collagen, using collagen as sole binder results in even higher CCS but also higher AP compared to tannin. Furthermore, the tannin-containing samples show a lower amount of fugitive compounds resulting in a lower mass change compared to the samples containing collagen.

CONCLUDING REMARKS

In the present study, environmentally friendly MgO-C refractories containing fused MgO raw material, MgO-C recyclates, environmentally friendly pitch- and resin-free binder systems containing lignin, collagen, or tannin as well as polyethylene glycol or fructose as pressing agents and citric acid as cross-linking agent were developed and characterized. Selected physical and mechanical properties of the developed refractories were compared to a pitch-and resin-bonded reference batch containing no recyclates.

The replacement of pitch and resin by environmentally friendly binders such as lignin and collagen results in a significantly lower bulk density, loss of CCS, and increase in AP. The comparison of the environmentally friendly binders reveals a slight advantage of adding collagen compared to lignin regarding the CCS while applying lignin as a binder results in a slightly lower AP. The combination of using a higher amount of fructose (2.4 wt.-%) and the abdication of polyethylene glycol results in significantly higher CCS and lower AP. The addition of citric acid (0.3 wt.-%) results in a significant increase of CCS and a decrease of the AP of approx. 20 % of the environmentally friendly bonded batches containing MgO-C recyclates which even exceeds the properties of environmentally friendly bonded recyclate-free batches without citric acid. Furthermore, it has been found that the recyclate-free MgO-C samples can be bonded with 0.6 wt.-% collagen and if used a proper amount of fructose (2.4 wt.-%) one can receive a CCS that is almost 90 % of the CCS of the resin-/ pitch-bonded reference batches. The addition of 0.3 wt.-% citric acid further improves the properties resulting in a CCS of a batch containing even MgO-C recyclates and an environmentally friendly binder that is only 5 % lower than a recyclate-free batch and only 15 % lower than a recyclate-free and conventionally bonded standard batch[10]. The effect of tannin as the sole binder overall resembles the effect of collagen, but the tannin samples exhibit a lower CCS compared to collagen, while their AP and mass change are lower.

In future studies, the DSC/TG behavior of the pure binder systems without MgO and C will be investigated. Additionally, thermo-mechanical properties such as hot modulus of rupture (HMOR) and refractoriness under load (RuL) will be determined as well as microstructural analysis on the most promising batches will be performed. Furthermore, the interaction with a steel melt will be investigated.

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