A Non-Hazardous PAH-Free Ramming Paste Binder Made from Wood

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Abstract

Ramming paste used in aluminium electrolysis pots requires specific properties and careful installation by workers to ensure reliable operation. Polycyclic Aromatic Hydrocarbons (PAH) in ramming paste made with coal tar binders have long been a concern in terms of health, safety and environment. Non-hazardous binders are needed that can be readily optimized by ramming paste producers for different aggregate types. This paper reports a new ramming paste binder developed from lignin: an abundant component of wood, rich in carbon. The binder is readily prepared by dissolving the lignin powder into water. The dry form of the lignin powder enables convenient storage and shipment, and ramming paste producers have the flexibility to optimize lignin-water ratios to suit specific aggregate types. The key physico-chemical properties of ramming pastes produced with lignin binders are presented and compared to typical worldwide ranges. This study demonstrates lignin as a convenient, flexible, and non-hazardous binder that can replace coal tar pitch in ramming paste.

Keywords: PAH-free cold ramming paste, Eco-friendly binder, Aluminium electrolysis pots, Hygiene, Environment.

1. Introduction

Aluminium electrolysis pots, or electrolytic cells, use ramming paste as a sealant to prevent fluid metal penetration into the inner parts of the cathode blocks or refractory, which can affect the pot's longevity. Proper installation of ramming paste is crucial to avoid technical and quality issues and is often considered essential for improved operations, as each pot consumes several tons of ramming paste [1]. The primary requirements for ramming paste in aluminium electrolysis cells are to ensure low shrinkage after solidification, which is largely influenced by the granulometry of the paste, appropriate rammability, neither too wet nor too dry, and minimal exposure to polycyclic aromatic hydrocarbons (PAH). Additionally, high thermal conductivity and resistance towards the deteriorating effect of sodium are essential [2].

Typical ramming paste consists primarily of dry aggregate, composed of calcined anthracite, calcined petroleum coke and/or artificial graphite, approximately 85 %, mixed with 15 % of a binder. A typical binder is coal tar pitch [3]. Under the European Union's harmonised classification and labelling system (ATP14), coal tar pitch is identified as potentially carcinogenic, capable of causing genetic mutations, and harmful to reproductive health, including risks to fertility and fetal development [4]. Emissions from coal tar pitch binder-based ramming paste during densification have raised concerns, specifically due to PAH, many of which are carcinogenic, like Benzo(a)pyrene (BaP), making ramming paste hazardous in terms of hygiene, health, safety, and environmental aspects [5].

Historically, ramming operations were carried out at elevated temperatures, around 120–150 °C, which led to significant PAH emissions and introduced operational stress due to the limited time window available for compaction to prevent the formation of laminations in the rammed lining. Over the years, ramming paste has improved significantly. Tepid ramming pastes allow for cooler ramming with reduced emissions, while cold ramming paste enables densification at near room temperature, limiting emissions and exposure, thus improving working conditions [6]. Eco-friendly cold ramming pastes with treated coal tar pitch binders to lower PAH content, and clean pastes using alternative binders with minimal or close to no BaP, have been developed [7]. This includes petroleum-based binders such as phenol-formaldehyde resins, which are polyaromatic thermosets with high carbon content, or biobased binders like molasses [8]. However, petroleum binders are expensive and have issues with emissions (e.g. formaldehyde), and biobased sugar binders have lower carbon content, impacting coke yield.

This paper discusses and describes the work done to evaluate the suitability of a new cold ramming paste binder, developed from lignin, which is an abundant component of wood, rich in carbon, namely lignosulfonates (LS). Lignosulfonate is a water-soluble, anionic polyelectrolyte polymer, typically derived from pulping of woody biomass. Lignosulfonates are created by the sulphonation of lignin and finds utility in multiple industrial applications. In refractories, lignosulfonates have been noted for their surface-active properties, making them useful as casting binders, dispersants, and plasticizers since at least the 1990s [9]. Lignosulfonates are safe to handle, non-hazardous when used industrially, and widely commercially available, with Borregaard being the world's leading producer of commercial lignosulfonate products from woody biomass [10]. Lignosulfonates are an excellent alternative to coal tar pitch as ramming paste binders due to their consistent year-round availability, high carbon content from aromatic structures, and resistance to microbial growth. They dissolve easily in safe solvents like water and glycol and are supplied as stable powders that can be mixed on-site to meet specific viscosity needs. Lignosulphonates are a 100 % biobased, ISCC PLUS certified biocircular material with a low carbon footprint. More importantly, they are also qualified as non-toxic, and non-hazardous by the Commission Implementing Regulation (EU) 2024/749. Their long history in refractory and ability to be tailored for specific applications further support their suitability as a modern, eco-friendly binder solution in the formulation of ramming paste used in cathode sealing and sidewall lining in Hall-Héroult electrolysis cells to produce primary aluminium.

1.1 Ramming Paste Made with Lignosulfonate Derived from Woody Biomass

One advantage of lignosulfonates, and the reason for testing multiple different products, is that they can be prepared to different specifications, meaning that there is a possibility to tailor-make products for different applications and requirements in terms of performance. Three lignosulfonate binders produced by Borregaard, a calcium based lignosulfonate labelled Ca-LS, and two different ammonium based lignosulfonates labelled AM-LS1, and AM-LS2 were sent to the research centre of R&D Carbon Ltd. (Figure 1, Left), in Switzerland, who conducted an evaluation including binder preparation, ramming paste production at the pilot scale with different binder contents and testing of the physico-chemical properties of the pastes after baking.

2. Experimental

2.1 Binder Preparation

Lignosulfonate is a powder product that firstly requires to be dissolved in water or other solvent (e.g. glycol, glycerol, etc) to become a binder. The viscosity of the binder can then be adjusted by the amount of added water. This will also impact its coking value, which is directly linked to the losses during the baking step.

For this purpose, mixtures of approximately 60–70 g were prepared with different ratios of water and lignosulfonate powder to estimate the required level to reach a typical viscosity of the resulting binder. The results are presented in section 3.1 The water was firstly heated to 60 °C and mixed with lignosulfonate for 10 minutes to obtain a homogeneous mixture. Additionally, the coking value and the ash content were measured to evaluate the binder quality.

2.2 Green Paste Preparation

To produce the different green ramming pastes at the pilot scale, an industrial semi-graphitic dry aggregate composed of 80 % of electrically calcined anthracite (ECA) and 20 % of graphite was used.

Dry aggregate mixtures, each weighing 5.5 kg, were prepared and preheated at 60 °C overnight. Additionally, approximately 1.5 kg of binder was prepared by mixing the lignosulfonate powder with a water ratio selected from the viscosity measurements previously performed.

The preheated dry aggregate was then placed into an intensive impeller mixer (Eirich, Germany), and the required amount of binder was added. After mixing for 10 minutes at 60 °C, the paste was removed from the mixer and allowed to cool down to room temperature. From this, 1 kg of paste was taken to evaluate its temperature window (Figure 1, Right), green apparent density and paste shrinkage, while the remaining paste was reserved for pilot electrode manufacturing.

Figure 1. Left: Dry aggregate preparation at the R&D Carbon research center, Right: RDC-194 ramming behavior equipment used for temperature window testing.

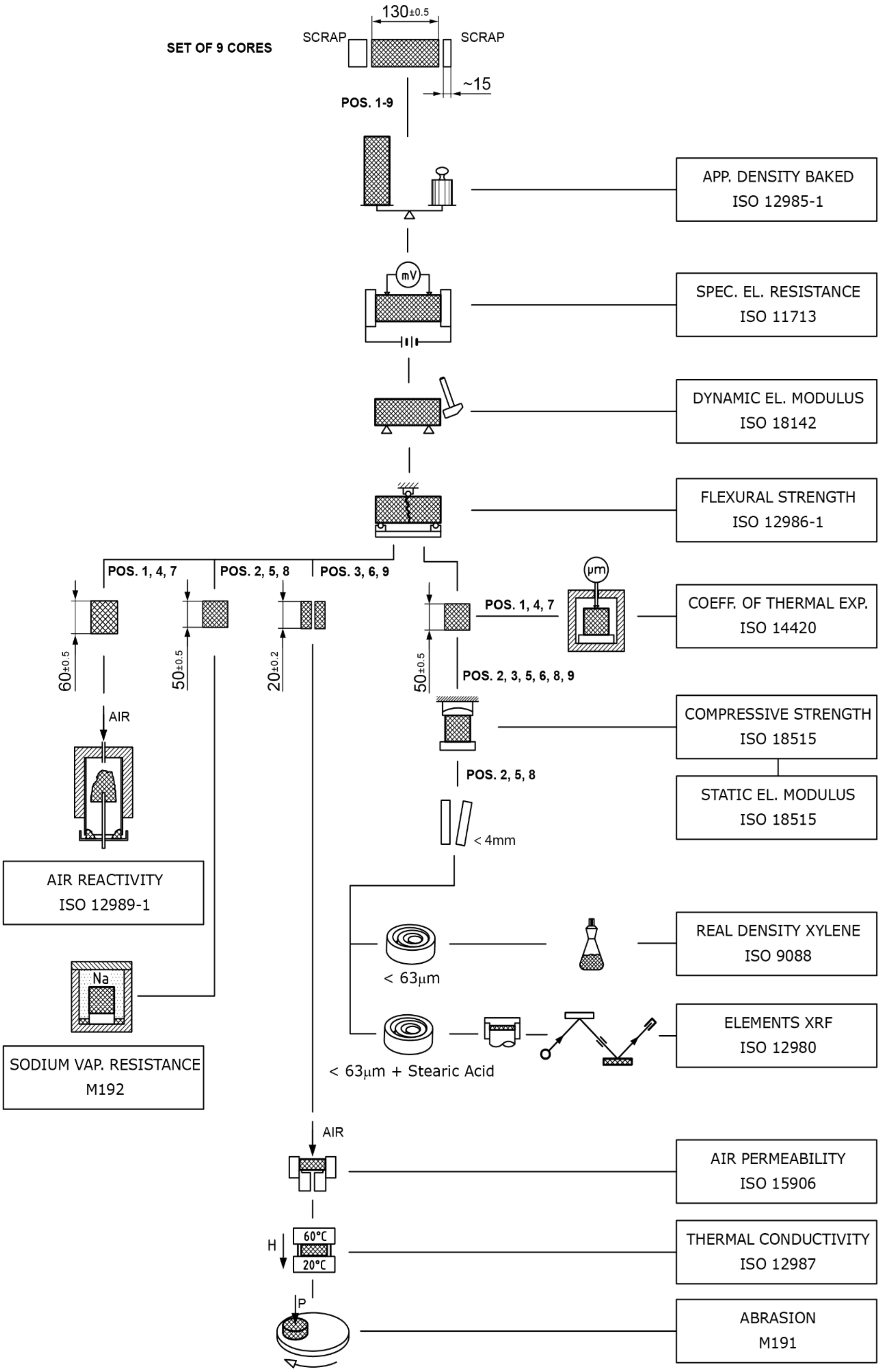

Figure 2. Test schedule for baked cores testing.

2.3 Pilot Electrode Preparation and Testing

The remaining paste that was reserved for pilot electrode manufacturing, was pressed at 350 bar to form green pilot electrodes. For each lignosulfonate and binder content, three batches were prepared, resulting in three pilot electrodes. These green pilot electrodes were then baked in an electrically heated furnace up to a final temperature of 1 100 °C. After baking, three cores per pilot electrode were drilled by using a pilot core drilling machine. The key properties of the baked pastes were then analysed according to the schematic illustration in Figure 2. For comparison purposes, one pilot ramming paste was also produced with a typical coal tar pitch binder.

3. Results and Discussion

3.1 Binders

Below, Figure 3 and Figure 4 show the correlation that was obtained between the viscosity, as well as the coking value, and the lignosulfonate content in the binder for two different types of lignosulfonates. It clearly demonstrates that a given viscosity can easily be targeted by adjusting the water to lignosulfonate ratio. However, an optimum ratio should be selected to obtain the best compromise between an acceptable viscosity and an as high as possible coking value.

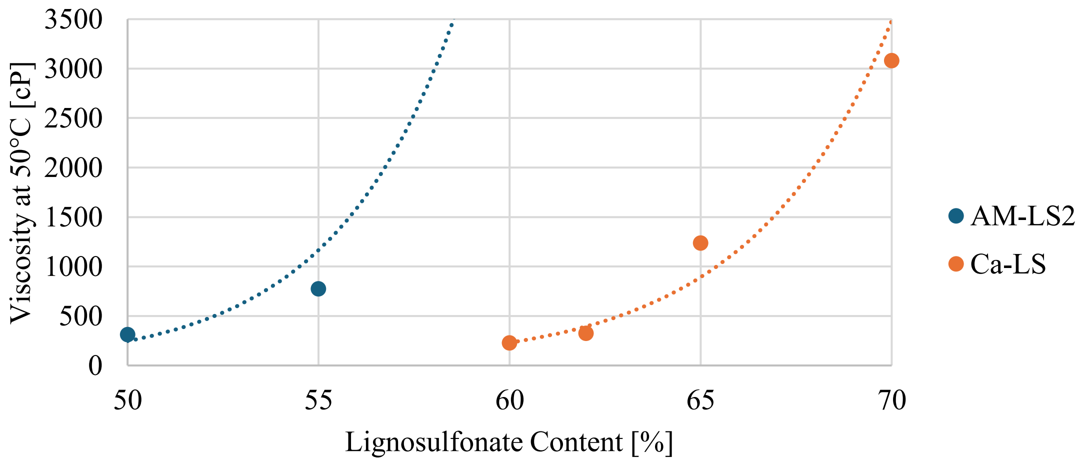

Figure 3. Viscosity value in function of the lignosulfonate content in the binder.

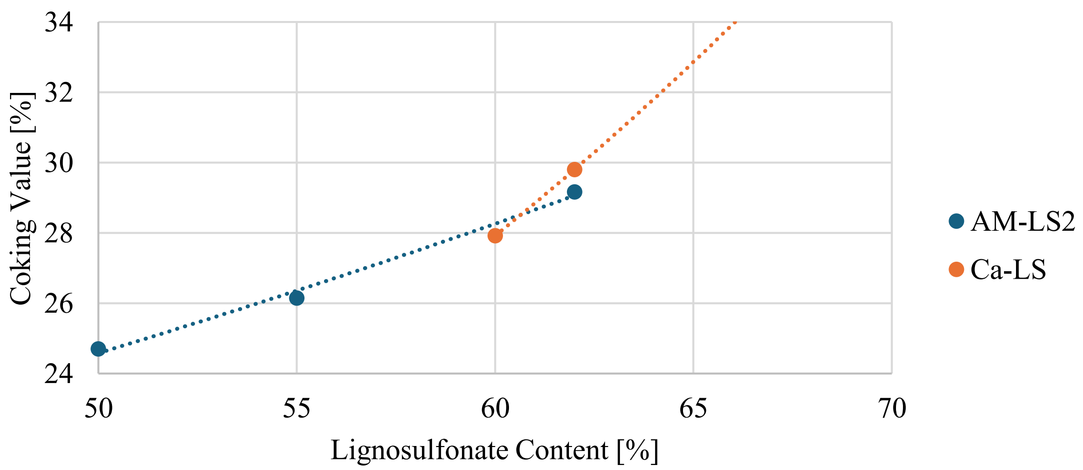

Figure 4. Coking value in function of the lignosulfonate content in the binder.

The properties of the binders with the selected water to lignosulfonate ratios for the pilot ramming pastes are shown in Table 1 and are compared to the ones obtained on the typical coal tar pitch. As no fine-tuning was done during this evaluation, different viscosity levels were achieved leaving potential for further optimization.

Table 1. Binder properties.

Property	Method	Typical coal tar pitch	Ca-LS	AM-LS1	AM-LS2
			62 % LS	62 % LS	55 % LS
Viscosity at 50 °C (Pas)	ASTM D5018	0.680	0.324	1.470	0.775
Coking Value (%)	ISO 6998	37	30	26	26
Ash Content (%)	ISO 8006	0.3	7.9	0.6	1.2

Overall, these results reflect very well the flexibility achievable by selecting a given lignosulfonate binder and by adapting the added water quantity. As expected with eco-friendly alternative binders, the coking values, indicative of the residual carbon after baking, were lower as compared to coal tar pitch. The ash content, reflecting the purity of the binder, is at a high level, i.e. close to 8 % for the lignosulfonate Ca-LS, while it remains quite typical for AM-LS1 with a value of 0.6 %.

3.2 Green Pilot Ramming Pastes

As a first assumption, green pastes with lignosulfonate were produced at the pilot scale with the same binder content (14 %) than the ramming paste with typical coal tar pitch. Based on the promising results, the binder content was increased to 16 % for the second batch to evaluate the impact on the properties. The results are shown in Table 2 and compared to the typical ranges for industrial PAH free pastes measured at the R&D Carbon Laboratory.

Table 2. Green pastes properties.

Property		Method	Standard Range for PAH Free Paste	Paste with typical coal tar pitch	Ca-LS		AM-LS1		AM-LS2	
					62 % LS		62 % LS		55 % LS	
Binder Content (%)		-	-	14.0	14.0	16.0	14.0	16.0	14.0	16.0
Temperature Window (°C)	Min	ISO 17544	5–25	20	14	11	26	16	8	7
	Max		25–45	42	34	27	58	32	34	21
Rammability at 25 °C	Max Density	ISO 17544	-	1.68	1.74	1.72	1.62	1.71	1.69	1.71
	N2		65–130	99	96	77	162	87	86	51

The evolution of the green density during compaction at room temperature, approximately 25 °C, and the expansion curves during baking (paste shrinkage evaluation) are shown in the Figure 5 and Figure 6. The rammability curves obtained with the lignosulfonate binders are well in line with the pitch-based ramming paste, except for the AM-LS1 paste with 14 % binder which requires higher ramming temperature. However, this was easily compensated by increasing the binder content to 16 %. The expansion curves show similar behaviour for all lignosulfonate binders with a shrinkage around 200–400 °C followed by a smooth expansion. This is quite different compared to pitch-based pastes, mainly due to different solidification temperatures and re-organization of the microstructure, but typical for industrial eco-friendly ramming pastes.

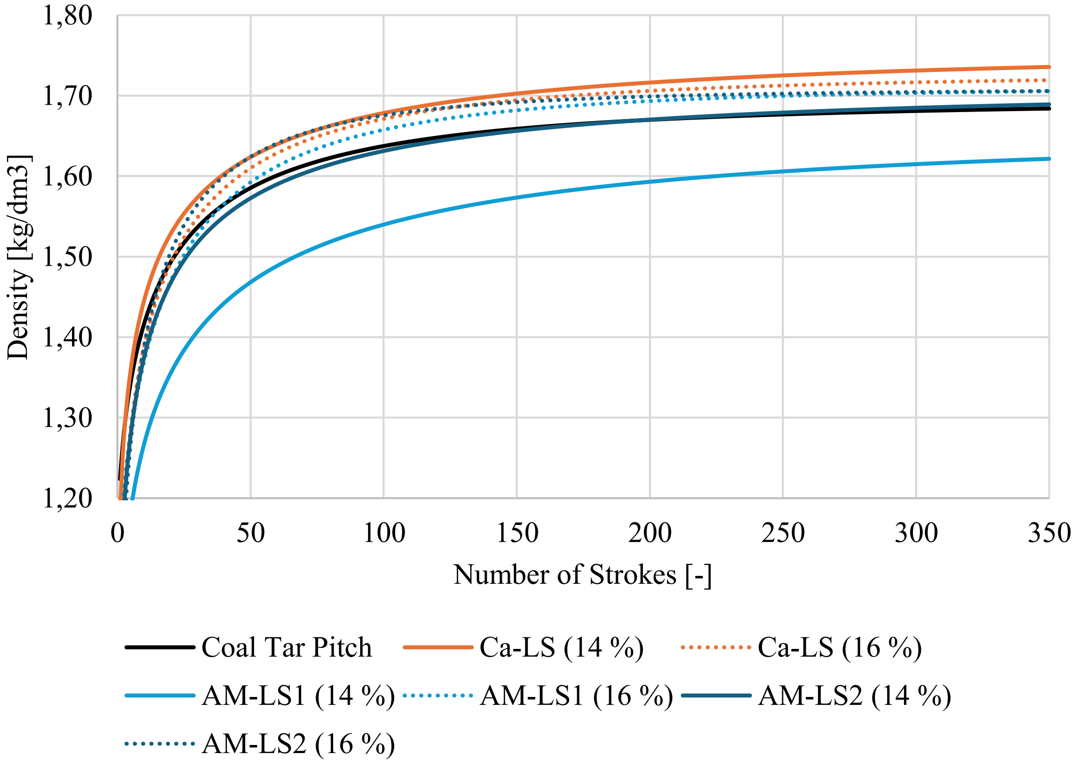

Figure 2. Rammability curves.

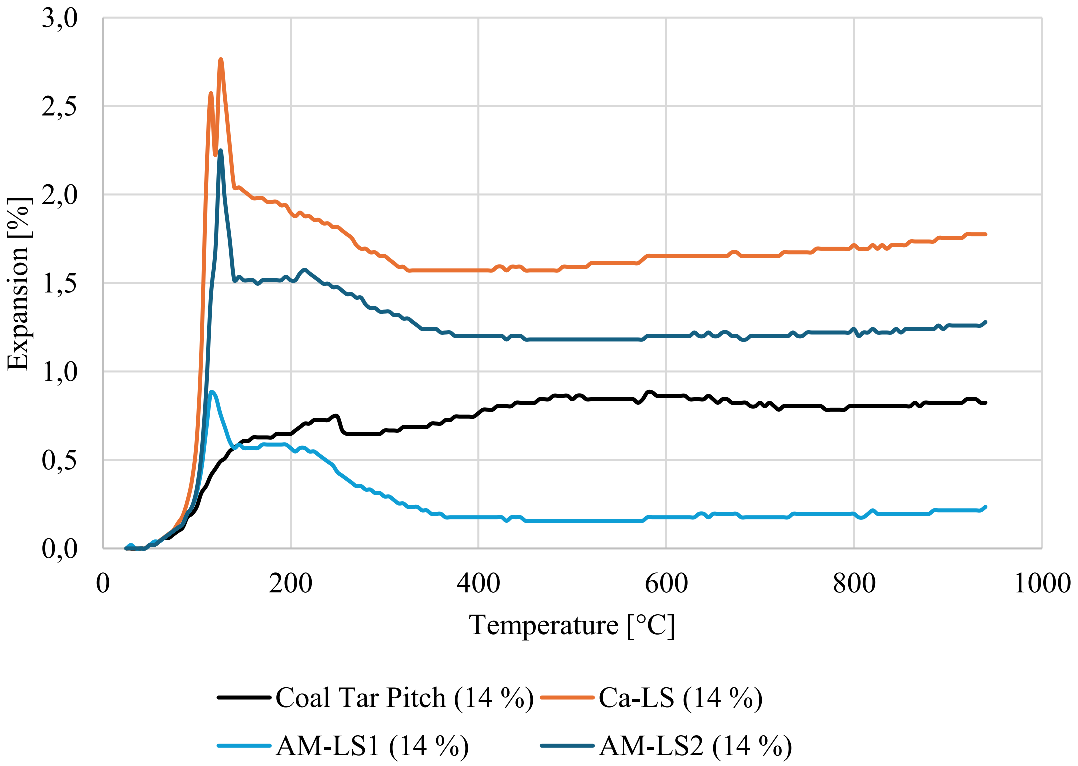

Figure 3. Expansion during baking curves.

3.3 Pressed Pilot Electrodes

The average results for the three different lignosulfonate binders at the most promising binder contents are presented in Table 3. This selection was based on the temperature window and rammability results measured on the green pastes. A level of 16 % of binder was selected for the AM-LS1 paste, while 14 % was selected for all the other pastes. The average results are compared to the typical ranges for industrial PAH free pastes measured at the R&D Carbon Laboratory and to the data obtained using a standard coal tar pitch binder with the same dry aggregate. The methods used for each measurement are listed in the Table 3.

Table 3. Average results of ramming paste properties at promising binder content.

Property		Method	Standard Range for PAH Free Paste	Paste with typical coal tar pitch	Ca-LS (62 % LS)	AM-LS1 (62 % LS)	AM-LS2 (55 % LS)
Binder Content (%)		-	-	14.0	14.0	16.0	14.0
Green Apparent Density of pilot shaped electrode (kg/dm^3)		ISO 12985-1	1.60–1.70	1.63	1.66	1.66	1.65
Baking Loss (%)		M131-1	9.0–13.0	8.2	9.5	11.1	10.3
Baked Apparent Density (kg/dm^3)		ISO 12985-1	1.40–1.50	1.49	1.51	1.47	1.49
Specific Electrical Resistance (µ·Ωm)		ISO 11713	60–80	87	69	59	63
Flexural Strength (MPa)		ISO 12986-1	2.0–4.0	2.7	2.0	3.7	2.3
Compressive Strength (MPa)		ISO 18515	13–22	12	15	17	14
Thermal Conductivity without contact paste (W/m·K)		ISO 12987	3.0–6.5	3.7	4.7	4.8	3.9
Abrasion (%)		M191	1–4	3	3	2	2
Sodium Vapour Resistance (%)		M192	40–90	-	61	63	62
Air Permeability (nPm)		ISO 15906	1.0–5.0	1.2	2.0	4.4	1.9
XRF Analysis	S (%)	ISO 12980	0.30–0.60	-	0.40	0.42	0.41
	Si (ppm)		0–20 000	-	2 508	2 651	2 502
	Fe (ppm)		1 000–6 000	-	2 648	3 056	2 918
	Al (ppm)		0–20 000	-	1 738	1 789	1 858
	Na (ppm)		100–500	-	806	276	343
	Ca (ppm)		100–2 000	-	5 359	2 161	2 247
	P (ppm)		40–600	-	26	34	43
	K (ppm)		200–1 200	-	461	408	414
	Mg (ppm)		200–1 800	-	772	743	791

Generally, all properties of the pastes made with the three lignosulfonate binders are well within the typical ranges for PAH free ramming pastes. As expected from the green paste evaluation, the green densities of the pilot anodes are higher than the one obtained with the pitch-based paste. Despite the low coking values of the binders, baked densities even on the high side of typical values are achieved and the losses during baking remain in the typical range as well. The specific electrical resistance and the thermal conductivity show a substantial improvement compared to the reference paste. The only property being negatively influenced is the air permeability, yet it remains within the acceptable range for PAH free pastes. As expected from the ash contents measured on the binders, the paste Ca-LS exhibits a higher contamination, mainly due to the presence of sodium and calcium.

The overall quality level that was achieved for these pilot pastes is remarkable, especially when considering that no-fine tuning was conducted leaving potential for further improvements.

4. Conclusions

Lignosulfonate is a bio-based and eco-friendly material that is nowadays available in industrial quantities and by nature rich in carbon. For these reasons, checking its potential usage as binder to produce ramming pastes used in the aluminium industry seemed obvious.

Three different types of lignosulfonate powders were evaluated through the production and testing of semi-graphitic ramming pastes at the pilot scale. The properties of the resulting green and baked pastes were compared to typical values for eco-friendly ramming pastes and to a paste produced with a typical coal tar pitch. The overall paste quality achieved has demonstrated that lignosulfonate is an excellent candidate to replace coal tar pitch in the production of ramming paste which could even be improved through further optimizations of the binder and paste preparations. It would also allow to easily meet a wide range of industry specifications by selecting the type of lignosulfonate and specific viscosity levels.

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