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

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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