



Green binder system for taphole clays: A potential for glycerine and phenolic resin

I.J-P. Cameron^{1,*} , A.M. Garbers-Craig

Centre for Pyrometallurgy, Department of Material Science and Metallurgical Engineering, University of Pretoria, Private Bag X20, Hatfield, Pretoria, 0028, South Africa

ARTICLE INFO

Keywords:

Taphole clay
Binder
green
Glycerine
Phenolic

ABSTRACT

Recent advancements in taphole clay binder development have focused on replacing toxic coal tar/pitch, which contains polycyclic aromatic hydrocarbons (PAH), with greener alternatives. In this study, three different taphole clays were prepared in the laboratory using different binder systems which include phenolic resin: 1) coal tar, 2) glycerine, and 3) petroleum waxy oil. The clays were evaluated and compared to the conventional coal tar and phenolic resin-containing clay used in platinum smelters. The evaluation methods employed included workability and extrusion pressure ageing, hardenability, strength development, and high-temperature properties, which comprised cold crushing strength after ageing at 200 °C, carbon yield, volatile organic compound concentration and apparent porosity. The results indicated that the preferred binder to replace coal tar was glycerine, as this clay retained both its plasticity and hardenability during ageing, while also attaining comparative strength development and high-temperature properties to those of the reference clay containing coal tar.

1. Introduction

The primary function of a taphole clay is to form a semi-permanent protective seal inside the tapping channel where molten material exits a smelter [1]. This material is considered granulo-viscoelastic as it consists of a mixture of either oxide and carbonaceous solid particles and a liquid binder [1–4]. Solid particles in a clay mixture are selected based on various factors, such as operating temperature, slag composition, anticipated wear from erosion, and thermal shock due to thermal cycling. The types of binder systems currently used for taphole clays include: 1) pitch-bonded, 2) resin-bonded, and 3) combination binders. Pitch-bonded clays utilize coal tar or coal tar pitch as a binder and are used for applications such as ferroalloy smelting (e.g., FeCr) [5]. Resin-bonded clays utilize phenol formaldehyde resin in either Novolac or resole form. This binder system is generally used for taphole clay in high-throughput blast furnaces that require short turnaround times between heats (casting durations) and experience higher degrees of erosion in the taphole [2]. The third binder system is a combination of both coal tar/pitch and phenolic resin. This binder system is used for both non-ferrous and ferrous smelting operations, allowing for better control over the performance of the clay by adjusting the ratios of these two constituents [3].

In most binder systems, coal tar or pitch is used as the primary binder, which provides both benefits and limitations to the taphole clay. Due to its relative high viscosity [6] compared to other binder types such as oils [5], tar/ pitch increase the plasticity of the clay. The complex composition of tar/pitch also results in a broad volatilization temperature range over which the clay can develop strength, forming fine pores that enhance high-temperature strength and leave residual carbon in the clay after heating [6]. However, the limitation of using tar/pitch is its high polycyclic aromatic hydrocarbon (PAH) content [6], which is more toxic than alternative aliphatic binders [6]. Therefore, alternative binders with lower PAH content are being investigated for use in taphole clay. Some of these include refined coal tar pitch (with higher boiling point PAH species removed), petrochemical binders and oils. The use of these binders helps to reduce the PAH content, however, most of them have chained hydrocarbon structures [6], resulting in a higher average mass loss over a narrow temperature range and lower carbon yield during heating in the tap hole. This compromises the high-temperature properties of the clay (i.e. corrosion resistance and high-temperature strength) due to an increase in porosity. In binder systems where tar/pitch is replaced with lower PAH alternatives, phenolic resin can help improve the strength of these clays. Using resin-bonded clays is another way in which the PAH content of the binder can be reduced [7].

* Corresponding author.

E-mail address: izakcameron@outlook.com (I.J-P. Cameron).

¹ Present address: Elkem Silicon Products, Materials Innovation, Fiskåveien 100, Kristiansand, Norway, 4621

However, one disadvantage of using phenolic-only binders is the reduction in clay adhesion as the resin begins to volatilize and cross-link at lower temperatures, which then decreases the extrudability and adhesion of clay to the inner part of the tapping channel [8].

The binder system of a taphole clay influences various performance indicators (extrusion pressure, taphole length, casting duration) and clay properties (taphole corrosion, sintering strength, molten metal/matte/slag splashing) [9]. Utilizing a combination binder system allows for better control over the above-mentioned properties and processes. The toxicity of the binders is commonly evaluated through an analysis of their 16-EPA-PAH content and by calculating their benzene equivalent (BE) from this analysis [10]. The term 16-EPA-PAH refers to a set of 16 polycyclic aromatic hydrocarbons (PAHs) that have been identified as priority pollutants by the U.S. Environmental Protection Agency (EPA) due to their toxicity and carcinogenicity, while the BE provides a measure for comparing the carcinogenic potency of organic substances. Previous work have shown that coal tar (BE = 1.67) has a higher PAH content than petroleum waxy oil (BE = 0.03) [6]. Phenolic resole resin as a binder in blast furnace taphole clay has also shown to have a lower PAH content than coal tar and coal tar pitch [7]. Glycerine has a primary alcohol structure that is aliphatic and hence does not contain any PAH. In this research, a combination binder system consisting of zero-PAH or lower-PAH binders (glycerine or petroleum waxy oil) together with phenolic resole resin was used in a taphole clay to assess the changes in both the performance indicators, such as extrusion pressure and casting duration, and high-temperature properties of the taphole clay. The rationale for using either glycerine or waxy oil as a replacement for coal tar/pitch is to investigate whether greener, low-PAH alternative binders can be used in taphole clays and to observe the associated changes in the material. The composition of the clay investigated in this research is designed for use in platinum smelting furnaces.

2. Materials and methods

2.1. Taphole clay preparation

Three different taphole clays were produced in the laboratory using a Hobart mixer with paddle beater to produce 15 kg samples for testing. The formulations used are given in Table 1, which include the oxide, carbide and carbonaceous raw materials, along with a lignin-substitute resole resin (ChemRes) and one of three binders: coal tar (reference binder) from the tar processing unit at ArcelorMittal, South Africa; research-grade glycerine (Clay A) from Sigma-Aldrich; or petroleum waxy oil from Sasol Limited South Africa (Clay B). The petroleum waxy

Table 1
Clay formulation with three different binders.

Raw material	Size range (mm)	Percentage (mass%)	Function
Calcined bauxite	3–5	16	Aggregate, abrasion
Calcined bauxite	1–3	17	Aggregate, abrasion
Calcined bauxite	+0.045–1	24	Matrix, abrasion
Calcined bauxite	–0.045	21	Matrix, sintering
Silicon carbide	–0.045	5	Matrix, abrasion
Clay (high alkali oxide content, carbon containing)	–0.045	12	Filler, sintering (liquid-state sintering)
Carbon (coal)	–0.045	5	Gas permeability, carbon network (strength)
Lignin/phenol-formaldehyde resole resin	-	+3.5	Low-temperature strength development
Liquid binder:	-	+16–17	Consolidating solid particles into a clay mass, plasticity, flowability
Coal Tar (Reference)	-	+13–15	
Glycerine (Clay A)	-	+13–15	
Petroleum waxy oil (Clay B)	-		

oil is a feedstock for production of green coke and diesel and primarily consists of aliphatic alkanes [6]. The designation of '+' indicates that the liquids were added in excess of the dry components of the clay, which total 100%. To achieve shear-thinning flow of the clay [11], the particle size distribution was designed with a distribution modulus of $q = 0.24$, according to the Andreasen model, shown in Eq. 1 [12].

$$CPFT = 100 \cdot \left(\frac{d}{D}\right)^q \quad (1)$$

where CPFT is the cumulative percent finer than particle size d , D is the largest particle size in the distribution and, q , the distribution modulus.

The mixing procedure for producing taphole clay differs from that of conventional monolithic refractories due to the higher viscosity of the binder. The dry mixture is homogenised in a mixer for 3 min. Thereafter, 50% of the liquid binder (coal tar, glycerine or waxy oil) is added and mixed for 2 min. After the first two minutes of wet mixing, the resin is added and mixed for a further 2 min. Three quarters of the remaining liquid is added and mixed until the wet clay reaches 45 °C. A sample of the wet clay is then taken, and its workability is measured. If the workability needs to be increased, a final addition of liquid is made at the discretion of the operator to achieve the desired workability. The clay is then placed in a container with a closed lid and stored at 23 °C.

2.2. Taphole clay evaluation

Three different taphole clays were prepared using three different binders and evaluated for changes in plasticity, extrudability, hardenability, strength development and high-temperature properties. Fig. 1 shows the different evaluations conducted on each of the clay samples and the conditions to which they were exposed and tested.

2.2.1. Plasticity and extrudability ageing

In this section, two properties of the clay being evaluated are described: plasticity and extrudability. Plasticity was assessed through workability (using a compactability test), while extrudability was evaluated by measuring the extrusion pressure.

The compactability test indicates how workable or formable the taphole clay is and how it compacts in the tapping channel after ageing and drying in the mud gun. Good compactability is desired, as it ensures proper closure of the tap hole [8]. The extrudability test indicates the pressure required from a mud gun to extrude the clay into the taphole. For any specific furnace, taphole clay will have a desired compactability and extrudability, expressed as a percentage, known as workability and extrusion pressure. Workability (or workability index) measures how well the clay maintains its shape and can be compacted once a load is applied, as in the case when it is rammed into the tap hole. Clay samples for workability measurements were prepared according to ASTM C181–11 (2018). Workability was evaluated using a AFS (American Foundry Society) rammer and cylinder with inner diameter of 50 mm. A 350 g clay sample was compacted on both ends of the cylinder 10 times and then removed from the cylinder. The compacted clay sample was then placed in the AFS rammer (without cylinder) and compacted 3 times to allow for unconstrained movement, determining the change in height before and after the 3 blows. This difference in height was calculated as a percentage reduction in height and was used to determine the workability. For these specific clays, workability was tested at 20 °C, with samples aged (in a closed container) for 21 days at 22 °C and tested intermittently, as shown in Fig. 1. For the clay considered in this study, the target workability is given as 38%, which is a function of the type of extruder/mud gun used for a specific furnace.

The extrusion pressure, also called the Marshall extrusion pressure (MEP) [3], is a measure of how much pressure is required to push the clay sample through an orifice, in this instance, the orifice of the mud gun during ramming or closing of the tap hole. A 450 g clay sample was placed inside the extruder cylinder-orifice configuration [3] (cylinder

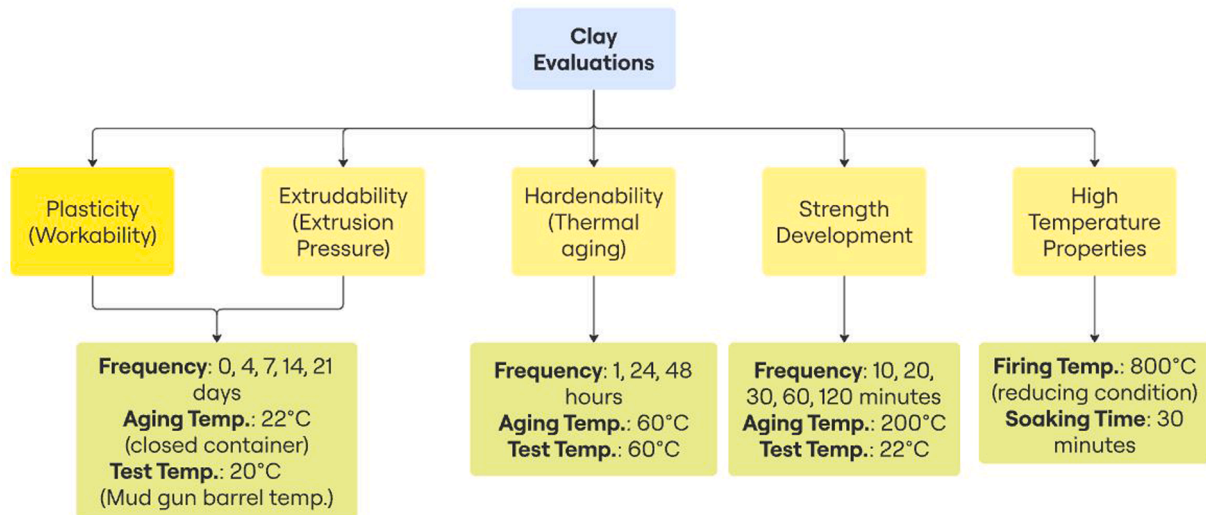


Fig. 1. Experimental setup and conditions for evaluating taphole clay samples from three different binders.

diameter = 50.7 mm; orifice diameter = 16.6 mm) and extruded through the orifice while measuring the maximum force needed to extrude the sample. The maximum force (L_M) reading was used to calculate the extrusion pressure (MEP) as shown in Eq. 2:

$$\text{Maximum pressure at die (MPa)} = \frac{L_M}{SA} \quad (2)$$

where SA is the curved surface area of the inner walls of the die in mm^2 . The extrusion pressure was measured after 21 days of ageing, similar to the workability test, and evaluated at 20 °C (average mud gun barrel temperature), with samples aged at 22 °C in a closed container.

2.2.2. Hardenability (plasticity and extrudability thermal ageing)

Hardenability refers to the decrease in adhesion of the clay when it is aged at a certain temperature. This simulates the scenario when taphole clay is heated in the mud gun over a period of time before ramming the clay into the tapping channel [9]. Excessive hardening of the clay, due to loss of low temperature volatiles in the binder, causes a reduction in adhesion of the clay to the refractory material in the tapping channel. It is largely influenced by the type of resin used and the low-temperature volatilization of the binder system when exposed to prolonged heating in the mud gun. Hardenability also consists of two properties, similar to the plasticity: workability and extrusion pressure. In this test, samples were aged at 60 °C for a total of 48 hours, and also tested intermittently, as shown in Fig. 1. The workability and extrusion pressure were evaluated at 60 °C, with the MEP configuration allowing for heating of the samples during analysis.

2.2.3. Strength development

Sample preparation for determining the strength development profile was similar to that used for workability testing. Five cylindrical samples (approximately 350 g, diameter = 50 mm, height = 120 mm) were prepared and evaluated at 200 °C. The selection of heating temperature depends on the binder system and is a function of the phenolic resin used, which may vary [13]. The cylindrical samples were heated for various times (Fig. 1) and removed from the oven to cool down before testing. The mass difference of the samples before and after heating was recorded to determine mass loss during heating. The cooled cylindrical samples were then tested for cold compressive strength (CCS) at 22 °C in accordance with ASTM C133–97 (2021).

2.2.4. High temperature properties

The high-temperature properties of the taphole clays that were

evaluated include volatile organic compound (VOC) content, carbon yield, CCS and apparent porosity (AP). Cylindrical samples similar to the workability samples were prepared, placed in a coke bed and heated to 800 °C for 30 min to prevent oxidation of the carbon material inside the clay. The samples were slow cooled in the furnace to room temperature, after which they were analysed. The carbon yield of the clay sample was tested in accordance with ASTM C571–81 using a Leco CS844 analyser. Apparent porosity was measured in accordance with ASTM C380–00, using Archimedes' principle.

3. Results and discussions

This section reports on the behaviour of the conventional taphole clay (reference) and the changes that occurred in both the process parameters and clay properties when alternative binders were used. The two alternative binder systems investigated were glycerine with resole resin (Clay A) and waxy oil with resole resin (Clay B). The reference clay sample utilized a combination binder system of coal tar with resole resin. All clays had the same resin content.

3.1. Plasticity and extrudability ageing

The workability and extrusion pressure ageing results are shown in Fig. 2. The workability specification is set at a minimum of 38% for the specific mud gun for which this clay is designed. This specification is important as a reduction in workability increases the MEP, resulting in difficulty extruding clay from the mud gun. This trend is evident in the results shown in Fig. 2. The reference clay experienced a 14.2% decrease in workability in 21 days. The extrusion pressure increased in the first 7 days as the workability decreased. The decrease in workability is more rapid in the first 7 days, after which it gradually decreases. For the reference clay, after 7 days the MEP decreased, which can cause bypass [14] of clay inside the furnace when more clay is pushed into the taphole than necessary. The desired MEP behaviour is a small increase in MEP during the first 7 days of ageing, followed by a plateau, as observed with Clay A and Clay B. For Clay A, there is a small increase in MEP in the first 4 days, followed by a plateau, with the smallest decrease in workability observed for this sample. For Clay B, workability decreases over the first 4 days and then unexpectedly increases. This can be attributed to the lubrication effect of the binder. During ageing of the clay, the liquid binder penetrates the open pores of the solid particles, which is a slow process due to the relatively high viscosity of the binders. Once the open pores are filled, any excess liquid causes slippage of particles relative to

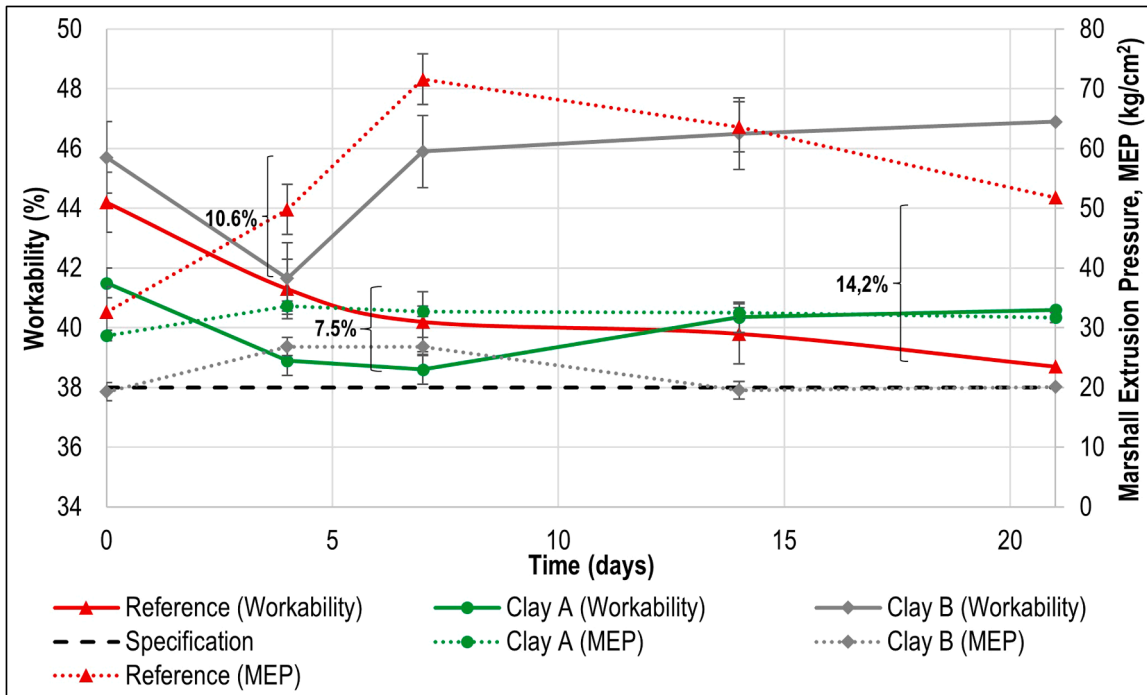


Fig. 2. Workability and MEP ageing of the three examined taphole clays (21 days ageing at 22 °C; test temperature 20 °C).

one another, which is observed in Clay B after 4 days of ageing. Clay A exhibits a similar trend after 7 days of ageing, though to a lesser extent.

3.2. Hardenability (plasticity and extrudability thermal ageing)

The hardenability of a taphole clay indicates the effect of extended heating at higher temperatures (60 °C) on the extrusion and workability of the clay. It is a function of volatile loss of the binder system, which causes an increase in viscosity and consequently an increase in extrusion pressure [3]. The extrusion pressure directly influences the taphole length and corrosion of the inner part of the tapping channel (closer to the inside of the furnace). During ramming, the mud gun extrudes clay

into the tapping channel with a constant pressure. If the clay hardens quickly, the same maximum extrusion pressure will be used, resulting in less material being rammed into the taphole and consequently, shorter taphole filling lengths. This can lead to increased corrosion on the inner part of the tapping channel as insufficient material is pushed into the taphole to coat and protect it.

During ramming of the taphole, the mud gun is exposed to elevated temperatures due to heat that radiates from the tapping launder onto the mud gun barrel. This increased heat causes low-temperature volatiles to be released from the binder, which increases the viscosity of the binder.

Thermal ageing results (Fig. 3) reveal that the reference clay loses almost half of its workability, resulting in a continual increase in

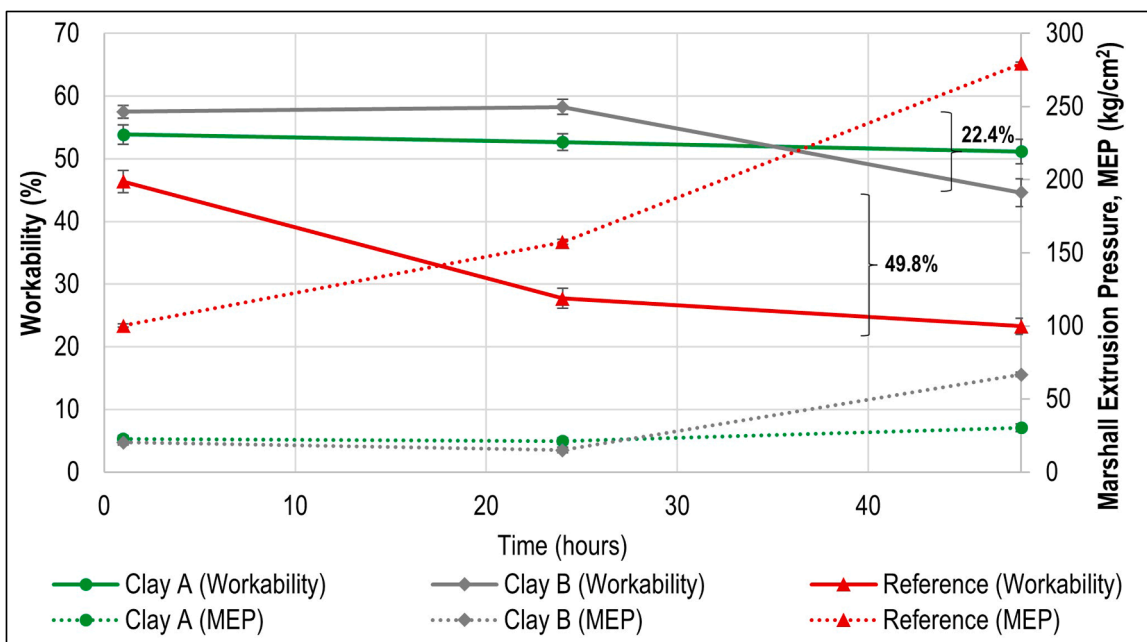


Fig. 3. Hardenability (thermal ageing) results of the three examined taphole clays (21 days ageing at 22 °C; test temperature 20 °C).

extrusion pressure. If the clay is heated for extended periods, this increase in extrusion pressure will lead to shorter tapping lengths. The workability of Clay A remained relatively constant, resulting in only a small increase in extrusion pressure. Clay B showed a decrease in workability of 22.4%, however, compared to the reference clay, this decrease only occurred after 24 hours of ageing. This decrease in workability caused an increase in extrusion pressure, however, the anticipated increase in extrusion pressure after 48 hours of heating would be significantly less for both Clay A and Clay B, compared to the reference clay.

3.3. Strength development

The strength development of a taphole clay is important as it indicates the hardening rate during heating and the corresponding increase in low-temperature strength [13]. Factors that influence the strength development include the quantity and type of binder, heating rate and final temperature (200–400 °C) [13] [15]. The increase in strength with heating, shown in Fig. 4, can be attributed to the increase in viscosity of the binder as low-temperature volatiles are released up to the decomposition temperature of the binder, which is higher than 600 °C for pitch and approximately 300 °C for resole resin. The resin in the clay imparts low-temperature strength up to the point where sintering begins at higher temperatures.

The resin selected for evaluation in taphole clay in this study has a curing temperature of approximately 200 °C. Therefore, the heating temperature for the samples in Fig. 4 was set at 200 °C. The volatile release of the samples during heating is shown in Fig. 4, where the masses before and after heating for the stipulated times (Fig. 1) were recorded to investigate the effect of binder volatilization on strength development.

The results in Fig. 4 show similar strength development trends for the reference clay and Clay A, namely a progressive increase in CCS as heating time is prolonged. There is a relaxation in CCS between 30–60 min in Clay B, which can be attributed to the slow cross-linking kinetics of the phenolic resin in the binder, as the temperature is close to the

curing temperature of the resin (200 °C). The continual increase in CCS is desirable as it fulfils two requirements: (1) it ensures that the taphole seal is formed as quick as possible, and (2) it allows for quick drilling. The latter is dependent on the final CCS value after 120 min of heating, as higher CCS can increase in drilling time during taphole opening. Other related issues, such as increased taphole wear [14] due to high molten flow rate or lancing if taphole clay sintering causes difficulty with opening, can also occur. Damage to tap hole refractories may result from excessive vibrations from drilling. For the platinum smelting furnace for which this clay is designed, the required final compressive strength at 800 °C is from 2.1 to 3.0 MPa.

The reference clay and Clay A achieved similar final CCS values after firing at 200 °C, but these values were lower than the specified limit of 2.1 MPa at 800 °C. Clay B showed a different trend, where after 15 min of heating, the CCS began to decrease. This reduction in strength at lower temperatures can affect the sintering strength of the clay at higher temperatures. A possible reason for this downward trend could be poor wettability and adhesion between the oxide particles and waxy oil binder, resulting in an inhomogeneous clay mass after mixing [3].

The volatile release from the reference clay and Clay A (expressed as % mass loss) shows a good correlation with strength development (Fig. 4) [13]. These two samples exhibit a gradual increase in mass loss as the CCS increases. For Clay A, the mass loss was the highest, while Clay B showed the lowest. Between 30 and 120 min, the mass loss of Clay B increased by 0.51%, compared to more than 1% for both reference clay and Clay A. The lower CCS of Clay B after heating is due to its lower rate of volatilization [6]. This lack of volatilization with extended heating time causes the viscosity to remain constant. As a result, the transition from liquid to semi-solid and finally to solid does not occur as readily with this binder system. As previously mentioned, the decrease in strength development can affect high-temperature strength and, as a consequence, may result in the spontaneous opening of the tap hole when a load (caused by the hydrostatic pressure of the molten material in the furnace) is applied to the sintered clay in the tapping channel.

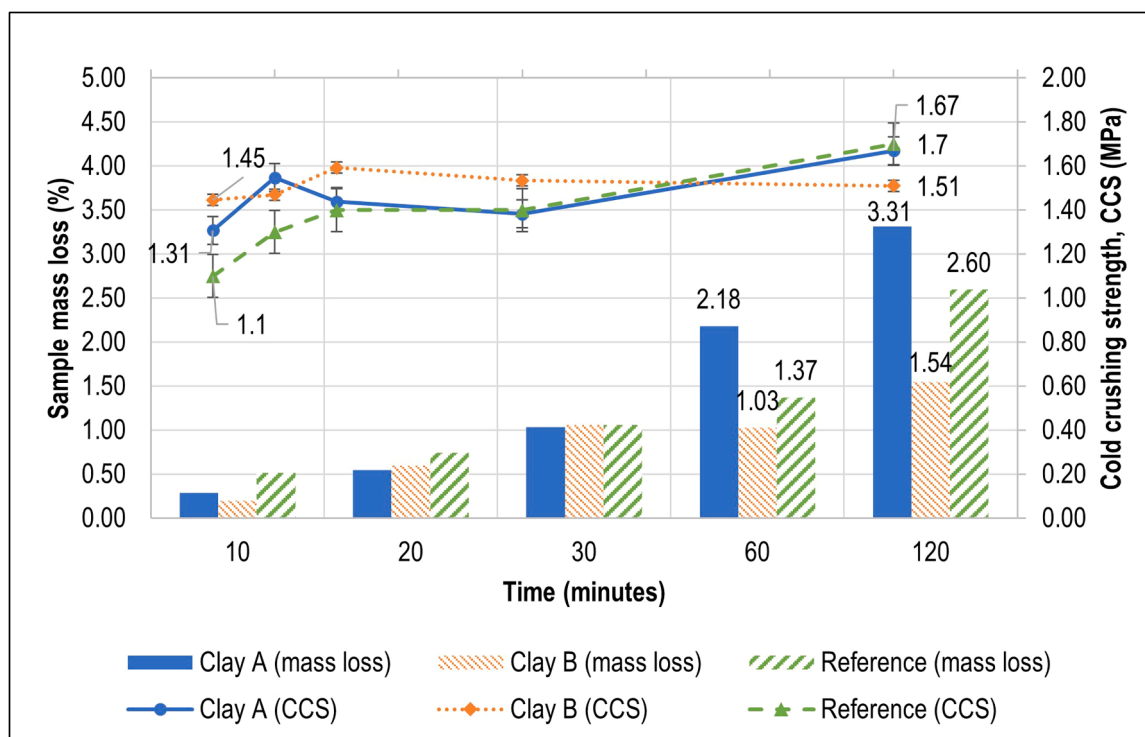


Fig. 4. Strength development profile and associated mass loss at 200 °C of the three examined taphole clays.

Table 2
High temperature (800 °C) properties of the three examined taphole clays.

Property	Reference clay	Clay A	Clay B
Volatile organic compound (VOC) (%)	21.3	14.6	13.8
Carbon yield (%)	12.4	10.3	11.2
Cold crushing strength (CCS) (MPa) (> 2.1 MPa)	3.1	2.4	-
Apparent porosity (AP) (%)	12.3	12.0	-

3.4. High temperature properties

The VOC concentration, retained carbon (% carbon yield), cold crushing strength and apparent porosity after firing at 800 °C under reducing conditions for 30 min for the examined taphole clays are shown in Table 2. The results indicate that Clay B did not maintain its integrity for testing after firing, as the sample crumbled in the furnace. This outcome was expected based on the strength development profile of Clay B.

The carbon yield in Table 2 reflects contributions from the solid carbon in the clay, the binder and the resin. For Clay A and Clay B, the carbon contribution from the binder is mainly due to the carbonization of the resin, given the low carbon yield of these binders [6]. The reference clay had a higher VOC concentration and carbon yield than the other clay samples. Clay A had the lowest carbon yield, however, it still retained its shape to achieve a CCS of 2.4 MPa after heat treatment at 800 °C. The reference clay exhibited a higher CCS (3.1 MPa), likely due to the relative higher carbon yield. For the PGM smelter for which this clay is being developed, a minimum high-temperature strength of 2.1 MPa is required to ensure that the clay can withstand the molten load in the furnace. Due to the lower CCS of Clay A compared to the reference clay, it is anticipated that Clay A will result in shorter drilling times because of its lower sintering strength. The apparent porosity of the reference clay and Clay A were comparable, although the Clay A sample had a higher mass loss, which did not seem to influence the strength of the clay.

The results in Table 2 show the effect of substituting coal tar/pitch in taphole clay with alternative binders and highlight areas for improvement. The temperature range in which a binder increases its viscosity below 200 °C is a critical factor in ensuring sufficient low-temperature strength development that translates into high-temperature strength. Another observation is the slight reduction in carbon yield. While this reduction is one of the factors influencing the high-temperature strength of the clay, its effect is evident in the difference in CCS values. Therefore, when substituting the binder for coal tar in taphole clay, adjustments to the binder-to-resin ratio are required to compensate for the reduced carbon yield and lower CCS. The extent of these adjustments depends on the specific furnace load requirements for the clay.

4. Conclusions

This study evaluated the effect of replacing high-PAH coal tar with a zero-PAH or lower-PAH alternative binder on the performance indicators and properties of a taphole clay intended for use in a platinum smelter. The following conclusions can be drawn:

- 1) Simulated tests for ramming, extrusion, and strength development indicated that Clay A (glycerine and resole resin) was the most suitable replacement for coal tar in taphole clay. Clay A showed the smallest decrease in workability ageing, the smallest increase in MEP, and the lowest hardenability.
- 2) Strength development trends revealed Clay A developed strength during heating similarly to the reference clay (coal tar), though with a higher mass loss over the heating period. Clay B did not show a sufficient increase in strength development, which was attributed to the limited mass loss that occurred in the binder during heating.

- 3) High-temperature testing revealed that Clay B did not maintain sample integrity, which is related to insufficient strength development at lower temperatures. The reference clay and Clay A had comparable compressive strength values after firing at 800 °C of 3.1 MPa and 2.4 MPa, respectively, despite Clay A experiencing a higher mass loss during strength development. The reference clay sample had the highest carbon yield and VOC concentration. The carbon yield results for Clay A and Clay B indicated a decrease in high-temperature strength due to the lower carbon yields of these binders.
- 4) Among the binder systems examined, the most suitable replacement for coal tar in taphole clay was found to be a combination binder system of glycerine and phenolic resin.

CRedit authorship contribution statement

I.J.-P. Cameron: Writing – review & editing, Writing – original draft, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **A.M. Garbers-Craig:** Writing – review & editing, Supervision, Resources, Funding acquisition.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Izak Cameron reports financial support was provided by Anglo American Platinum. Izak Cameron reports a relationship with Anglo American Platinum that includes: funding grants. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- [1] E.Y. Sako, D. Galesi, C. Leão, F.A. Rodrigues, M.A. Souza, J. Roy, M. Kitamura, T. Horiuchi, High-performance taphole clay: A key for blast furnace hearth protection and a tool for cost reduction, *Iron Steel Technol.* (2018) 82–87.
- [2] M. Kitamura, Optimizing Taphole Clay technology, *Shinagawa Techn. Rep.* 57 (2014) 1–4.
- [3] I.J.-P. Cameron, Investigating premature ageing of blast furnace taphole clay containing a resole resin and liquid pitch binder. MEng(Metallurgy), University of Pretoria, Pretoria, 2021. <http://hdl.handle.net/2263/78314>.
- [4] K.R. Siva, M. Raffi, R.K. Srinivasa, Experimental study on environment friendly taphole clay for blast furnace, *ICRAMMCE 2017, IOP Conferen. Ser.: Mater. Sci. Eng.* 330 (2018) 012056, <https://doi.org/10.1088/1757-899X/330/1/012056>.
- [5] T.M. De Oliveira, W.M. Silva, H.C. Bassalo, A.S. Ribeiro and M.A. dM. Brito, Taphole clay technologies for ferroalloy reduction furnaces, *Furnace Tapping 2022 Conference, February 27 – March 3 2022, Anaheim, California, USA, 365–374.* doi:10.1007/978-3-030-92544-4_27.
- [6] I.J.-P. Cameron, S. Ramjee, A.M. Garbers-Craig, Comparative study between coal tar pitch and lower polycyclic aromatic hydrocarbon (PAH) alternative binders for use in taphole clays, *Open Ceram.* 16 (2023) 100470, <https://doi.org/10.1016/j.oceram.2023.100470>.
- [7] G. Copetti, Blast furnace taphole clay and cast house - A greener approach, in: *8th International Conference on Refractories, Jamshedpur (ICRJ), India, 2024*, pp. 98–101, 14 & 15 March.
- [8] Y. Otsubo, A. Yamasaki, Y. Tanaka, T. Matsunaga, High performance taphole clay for blast furnace, *TRL Krosaki Refractor.* (2010) 1–8. <https://www.scribd.com/document/522181655/IREFCON-2014-Taphole-Clay-for-Blast-Furnace-Dc55f353a0-2#>.
- [9] I.J.-P. Cameron, A.M. Garbers-Craig, Understanding how the binder system influences the properties and process performance indicators of taphole clays, *Refractor. Worldforum* 16 (2024) 28–31.
- [10] E.I. Andreikov, I.S. Amosova, M.G. Pervova, Determining the content of polycyclic aromatic hydrocarbons in industrial samples of coal tar and pitch, *Coke Chem.* 51 (8) (2008) 321–325.
- [11] A. De Pretto and L. Lindstad, Health-friendly plugging repair paste, *Furnace Tapping 2022 Conference, February 27 – March 3 2022, Anaheim, California, USA, 375–387.* DOI:10.1007/978-3-030-92544-4_28.
- [12] S. Otraj, S. Marzban, Z.A. Nemati, N. Sajadi, M.R. Nilforoushan, Behaviour of alumina-spinel self-flowing castables with nano-alumina particles addition, *Ceram. - Silikáty* 2 (53) (2009) 98–101.

- [13] T. Kageyama, M. Kitamura, D. Tanaka, Shinagawa Technical Report, no. 46, 2005, pp. 41–46.
- [14] R.L. Nelson, R.J. Hundermark, The tap-hole - key to furnace performance, *J. South. Afr. Instit. Min. Metall.* 116 (2016) 465–490, <https://doi.org/10.17159/2411-9717/2016/v116n5a12>.
- [15] S.A. Nightingale, L. Wells, F. Tanzil, J. Cummins, B.J. Monaghan, K. Price, Assessment of the structural development of resin bonded taphole clays, in: ICSTI 06, International Conference on the Science and Technology of Ironmaking, ISIJ, Osaka, Japan, 2006, pp. 251–255. <https://ro.uow.edu.au/engpapers/1226>.