Premature ageing of a blast furnace taphole clay containing resole resin and liquid pitch as binder

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Abstract

The cause of reduced workability and increased ageing of a blast furnace taphole clay was examined. The investigated taphole clay contained 60 mass% alumina, with phenol-formaldehyde resole resin and liquid pitch serving as the binder system. The workability and Marshall extrusion pressure of the as-manufactured clay samples were evaluated to assess the extent of ageing of the clay. The wettability of all the raw materials was investigated to confirm compatibility between the dry raw materials and both the resin and liquid pitch, while the dry raw materials were analysed using XRF, XRD, and SEM-EDS. The characterisation of the resin and liquid pitch, as well as an analysis of their interaction, was performed using viscosity measurements, Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). The analyses confirmed a chemical interaction between the resole resin and liquid pitch, where the chemical structure of the resole resin changed when mixed with pitch, preventing the typical curing behaviour of the resin. Upon ageing of the resin-pitch mixtures, the resin underwent premature cross-linking, causing the curing process to initiate at lower temperatures, i.e., earlier onset of curing. This premature cross-linking was likely due to secondary amines present in the liquid pitch, which acted as a catalyst for the curing process of the resin. This reduction in curing temperature after ageing was confirmed by an increase in binder viscosity, which was identified as the primary cause of reduced workability, accelerated ageing, and increased Marshall extrusion pressure of the taphole clay.

Keywords

taphole clay, phenol-formaldehyde resin, liquid pitch, workability, Marshall extrusion pressure

Introduction

Blast furnace taphole clay has been used for decades with little change to the primitive raw materials and binders it employs. Recent developments have explored the use of cheaper alternative raw materials as aggregates to reduce the cost of the clay, as well as tar-alternative binders that are less harmful to both the environment and operators who manufacture or use the material (Rosch, 2019). A key objective of these developments was the creation of a more environmentally friendly "green" taphole clay, which led to the present investigation.

The change in the binder introduced in this product development involved replacing the conventional high-volatile tar and resole resin combination with a synthetic liquid pitch and resole resin. However, a problem was identified with this new binder system: premature ageing of the clay, which manifested as a crumbling effect and reduced workability. The objective of this investigation was therefore to determine why this new binder combination caused the clay to age prematurely.

Several factors influence the ageing and workability of taphole clay, including the particle size distribution (PSD) of individual raw materials; the solubility of aggregate and matrix raw materials in the binder or binder combination; impurities in the aggregates and matrix (such as lime and sulphur); ageing temperature; and the viscosity of the binder, which is in itself influenced by temperature and the degree of cross-linking (Nelson, Hundermark, 2014).

The PSD of both the individual raw materials and the overall mixture affects the rheological behaviour of the clay. Any rheological change, in turn, impacts the workability of the taphole clay (Adeyinka et al., 2009). The solubility of the aggregate and matrix raw materials in the binder or binder mixture also influences workability through polar-polar or nonpolar-nonpolar interactions between the solids and the binder(s). The polarity interactions, whether liquid-liquid or liquid-solid, determine whether the clay remains well mixed or separates upon ageing (Lin et al., 1993). Mismatched polarities between the binder components can lead to reduced workability and increased ageing.

The viscosity of the binder or binder combination is affected by both temperature and structural changes caused by cross-linking. As the binder undergoes structural changes during cross-linking, its viscosity increases, leading to a reduction in workability (Li et al., 2018; Moritz, 1989). Premature cross-linking of the resin in the binder accelerates the curing process (Laza et al., 2001), causing a premature increase in binder viscosity, which reduces workability and increases ageing of the taphole clay. Certain impurities, such as lime or sulphur, associated with the raw materials, can also catalyse cross-linking of the resin in the binder (Young, Lovell, 1991).

During the synthesis of resole resin, phenol reacts with formaldehyde under basic conditions to form an addition compound (due to chemical addition), followed by a condensation reaction. This condensation step produces methylene bridges with methylol functional groups in ortho or para positions (Laza et al., 2001). Due to the water present in the resole resin, various types of catalysts can be used for curing, including acids, bases, or amines (primary, secondary, and tertiary) (Laza et al., 2001). Hexamethylenetetramine (hexamine) is often used as a curing agent in resole-type resins.

Experimental procedure

This study was divided into three parts: In the first part, the properties of two taphole clays with different binder systems were studied. The second part focused on the aggregate and matrix raw material used to constitute the taphole clay, while the third part investigated the individual binders as well as different binder combinations. Tests performed on the taphole clays included workability, Marshall extrusion pressure, and viscosity. The aggregate and matrix materials were analysed for particle size distribution (PSD), polarity, wettability, and associated impurity components, while the binders and binder combinations were evaluated based on their structural and thermal characteristics.

Materials

The two taphole clay samples (Clays A and B) were prepared according to the formulation shown in Table 1 and in accordance with ASTM C1054-18 (2018) (Saeki, Tanaka, 1984). The amounts and size distributions of the aggregate and matrix materials used in taphole Clays A and B were similar, the only difference lay in their binder systems. The particle size distributions of Clays A and B were continuous, with no gaps that could negatively affect the flow properties of the clay when extruded or pushed through a mud gun. Taphole Clay A contained 17% liquid pitch and 1% resin, while Clay B only contained 18% liquid pitch and no resin. The aggregate and matrix materials accounted for 100% of the formulation by mass, with the resole resin and liquid pitch added on top of that amount. Hence, the designation “+100%” in Table 1.

The aggregate included bauxite and andalusite, while the matrix material comprised andalusite (ball mill fines), calcined clay (ball mill fines), and calcined alumina. Kaolinite was added as filler and sintering aid, coal was included to enhance gas permeability, and silicon carbide was added to improve abrasion resistance.

The binders used were resole resin and liquid pitch, as well as various combinations of the two binders (5.6% resin – 94.4% pitch, 25% resin – 75% pitch, 50% resin – 50% pitch, 75% resin – 25% pitch).

A defined protocol was followed for the ageing and curing tests. Binder samples were prepared by weighing the appropriate ratios of liquid pitch to resole resin and mixing them for 5 minutes. After mixing, the viscosities of the samples were measured, and the samples were analysed using Fourier-transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC). To simulate ageing, the samples were placed in an oven at 45 °C for two weeks. After this ageing period, the samples were re-analysed using the same techniques (viscometry, FTIR, and DSC). For the curing tests, the same protocol was followed, except that samples were cured at 130 °C for 4 hours to ensure complete curing of the resin.

Test methods used to study the taphole clay

The workability and Marshall extrusion pressure (MEP) of a taphole clay are closely related and therefore cannot be considered in isolation. Workability was assessed using the ASTM C181-11 (2018) test, which involves applying a load to a sample using a rammer and measuring the change in sample height. The MEP test was conducted using the configuration shown in Figure 1. A

Table 1

Taphole clay design used for both Clays A and B

Raw materials	Size range	Clay A (Mass %)	Clay B (Mass %)	Function
Bauxite	+45 µm to -1 mm	35	35	Aggregate
Andalusite	+45 µm to -1 mm	15	15	Aggregate
Andalusite (BMF)	-45 µm	7.5	7.5	Matrix material
Calcined clay (BMF)	-45 µm	7.5	7.5	Matrix material
Calcined alumina	-45 µm	5	5	Matrix material
Clay - kaolinite	-45 µm	10	10	Filler/sintering
Carbon - coal	-45 µm	5	5	Gas permeability
Silicon carbide	+45 µm to 0.8 mm	15	15	Abrasion resistance
Phenol-formaldehyde resin (resole)	–	+1	–	Strength development
Liquid pitch binder (a combination of high volatile coal tar pitch and heavy oils)	–	+17	+18	Binder/filler

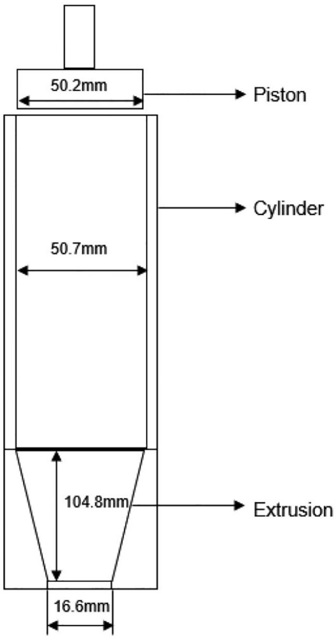

Figure 1—Schematic of the Marshall extrusion mould assembly

450 g taphole clay sample was weighed and heated to 45 °C in a water bath for 2 hours. The heated sample was placed into the cylinder of the assembly, and the piston positioned on top of the sample. The assembly was inserted into the Marshall test automatic extruder, and the maximum force exerted on the sample was recorded. The MEP was then calculated as the average value obtained from Equations 1 and 2. The constants used in both Equations were calculated based on the setup shown in Figure 1. The maximum pressure on the piston/die was expressed in MPa, where the maximum load was measured in kN and the curved surface area in mm².

$$\text{Maximum pressure at piston} = \frac{\text{Maximum load}}{\text{curved surface area of piston}} \quad [1]$$

$$\text{Maximum pressure at die} = \frac{\text{Maximum load}}{\text{curved surface area of die}} \quad [2]$$

Test methods used to characterise the aggregate and matrix materials

Wettability

The wettability of the aggregate and matrix materials with respect to polar (water) and non-polar (hexane) liquids was examined to confirm that there is no polarity mismatch between solid particles (i.e., fines and aggregate) and the binders (i.e., resin and liquid pitch). The polarity match between binders and particulates is important for two reasons. Firstly, the solubility of the resin in the pitch is highly dependent on the polarity of the compounds it contains and its molecular mass distribution (Li et al., 2000). A polarity mismatch may cause problems with the mutual solubility of the resin and pitch, as well as their interaction with the particulates in the clay (Lin et al., 1993). Secondly, a polarity mismatch between one of the particulate raw materials and the rest of the oxides, carbides, and binders may cause the clay to separate due to repulsive forces within the clay mixture. This separation can negatively affect the clay's workability over time.

The phenolic resin is considered polar because of its functional groups, but this is dependent on the ratio of phenol to formaldehyde (Li et al., 2000). The liquid pitch is also considered to be polar due to one of its major constituents being coal tar pitch. The coal tar pitch has hydroxyl and amino functional groups, which convey more polar behaviour to this liquid (Knicker et al., 1996; Kabe et al., 2004).

Wettability was evaluated using an Attention Tensiometer Sigma 700/701 in conjunction with Washburn's equation, to determine contact angles and wettability (Galet et al., 2010). During the wettability test, the sample was suspended in a test medium: water for the polar wettability test and hexane for the non-polar wettability test. The tensiometer recorded the change in sample mass over time. A mass2/time value was obtained from the slope of the mass versus time graph. Washburn's equation relates this mass2/time value to the contact angle:

$$\frac{m^2}{t} = C_W \frac{\rho_l^2 \gamma}{\mu} \cos\theta \quad [3]$$

Where C_W is a constant calculated for each sample, ρ_l the density of the test liquid in kg/m³, μ the viscosity of the test liquid in Pa.sec, γ being the surface tension of the test liquid, and θ the contact angle.

Mineralogical characterisation

Mineralogical characterisation was carried out to ensure the quality and to identify any impurities, such as lime or sulphur, that could attribute to cross-linking of the resole resin used in the binder. The mineralogical characterisation of the aggregates and matrix raw materials was done using X-ray fluorescence (XRF), X-ray diffraction (XRD) and scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) analyses. The crystalline phases present in the mineral aggregates were evaluated using XRD. Samples were pulverised and homogenised in accordance with the method described by Hanke (2017). The samples were loaded in accordance with the Panalytical backloading system and analysed using a PANalytical X'pert Pro powder diffractometer in θ-θ configuration with an Xcelerator detector and variable divergence and fixed receiving slits with Fe-filtered Co-Kα radiation (λ=1.789Å) (Chatterjee, 2001). The mineralogy and microscopic properties of the aggregate and matrix raw materials were investigated using SEM-EDS. Backscatter electron images were captured and point and area analyses performed to supplement the XRF and XRD analyses. The quantitative EDS analysis was conducted in accordance with the ASTM e1508-12a (2019) standard guideline. The coal aggregate was characterised in terms of ash, moisture, volatile matter, fixed carbon, and sulphur contents in accordance with the ASTM D3172-13 (2013), SANS 927:2013 (2013), ASTM D5373-16 (2016), and ASTM D4239-18e1 (2018) test methods, respectively.

Test methods used to characterise the binders and binder mixture

Viscosity

The viscosities of Clay A, the resole resin, the pitch as well as resin-pitch mixtures were measured using an Anton Paar Physica MCR301 equipped with a Peltier heating chamber and 50 mm plate spindle. The rheology of taphole Clay A was studied by measuring its viscosity at different temperatures over time. Each binder was characterised by measuring the change in viscosity as a function of shear rate to distinguish between Newtonian and non-Newtonian behaviour. The resole resin and liquid pitch binders used in Clay A were analysed to monitor cross-linking as a possible cause of ageing and reduction workability. Viscosity changes were also examined as a function of temperature, with samples heated from 30°C to 130°C at a heating rate of 10°C/min. Binder combination samples (5.6% resin – 94.4% pitch, 25% resin – 75% pitch, 50% resin – 50% pitch, 75% resin – 25% pitch) and aged binder combination samples (aged at 45°C for two weeks) were also tested for viscosity as a function of both shear rate and temperature over the same range.

FTIR/ATR

The resin, liquid pitch, and their combinations (as used in the viscosity measurements) were characterised using Fourier-transform infrared spectroscopy with attenuated total reflectance (FTIR/ATR). FTIR was used to identify the functional groups in the resin and pitch, and to detect any changes to these functional groups when the components were mixed and aged. FTIR/ATR analysis was employed to determine whether changes in chemical structure correlated with the observed viscosity variations in the mixed and aged samples as a function of temperature. Cured samples (130°C for 4 hours) were also analysed to track progressive changes in functional groups during mixing, ageing, and curing. These structural changes were then related to the observed viscosity trends. FTIR/ATR was conducted using a PerkinElmer spectrum 400 FT-IR, with samples placed directly onto the diamond cell for analysis. Background scans, as well as CO_2 and H_2O spectra, were removed from the sample spectra. Analyses were conducted at 25°C.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) was used to investigate the heat flow in the binders and their combinations (mixed, aged, and cured) as a function of temperature. DSC analysis supported the viscosity and FTIR results by identifying characteristic endothermic and exothermic transitions in the resin, pitch, and their combinations. A small sample of binder (approximately 20 mg) was placed in a 30 μL aluminium pan, sealed with a lid, and heated in a nitrogen atmosphere. Samples were heated at 10°C/min in air, with a gas flow rate of 20 mL/min.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed to measure mass changes in the virgin binders as a function of temperature. A 20 mg sample of either resin or pitch was heated in an alumina crucible using a TA Q600 SDT. Samples were heated from 30°C to 130°C in a nitrogen atmosphere, and mass loss was recorded. The heating rate was 10ºC/min, with a nitrogen flow rate of 20 mL/min.

Results and discussion

Properties of Clays A and B

This section describes the behaviour of the two examined taphole clays.

Workability and MEP of the taphole clay

Workability decay curves of taphole Clays A and B at 35°C, together with their workability specifications, are shown in Figure 2. Both clays exhibited an initial decrease in workability, with Clay B reaching a plateau at 33% (starting from 36%) after 14 days. In contrast, the workability of Clay A declined to 26% (also starting from 36%) after 21 days, corresponding to a 28% reduction. Clay B showed a workability loss of only 8%. These results suggest that the resole resin in Clay A significantly reduces the workability of the clay.

The MEP results (Figure 3) show a trend similar to that of the workability results. Over a period of 21 days, the load per unit area required to push the clay through an orifice increased for both Clay A and Clay B, with Clay B starting to plateau after 7 days. In contrast, the MEP of Clay A increased past 21 days. The constant increase in MEP of Clay A is indicative of a possible problematic operation of a mud gun as the taphole clay is pushed through with increasing difficulty. The samples for both workability and MEP were tested according to non-standard procedures. Based on experience of previous measurements the variability in the technique is approximately 2%–5% for workability and 5%–10% for MEP (Cameron, Garbers-Craig, 2025).

Binder viscosity changes

The workability decay results of clays with different binder viscosities are shown in Figure 4. These results indicate that, as the binder viscosity increases, the workability decay of the taphole clay increases. This confirms that lower-viscosity binders facilitate easier filling of the tap hole, although this does not account for the performance of the clay as a refractory material. A clear difference in workability reduction is observed between Clay A, which contains both resin and liquid pitch, and Clay B, which contains only liquid pitch (Figure 2). These results suggest that a mechanism contributing to the workability decay in resin-pitch mixtures likely involves an increase in viscosity.

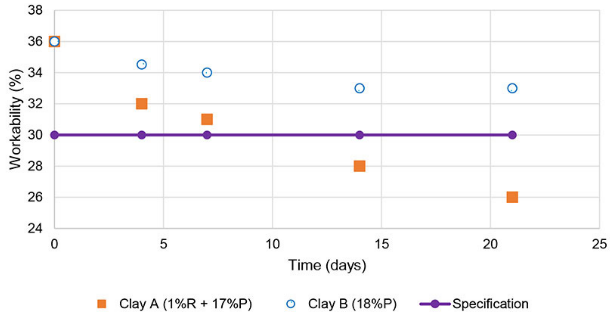

Figure 2—Workability ageing of Clays A and B (R =Resole resin; P = Liquid pitch; Test temperature 35°C

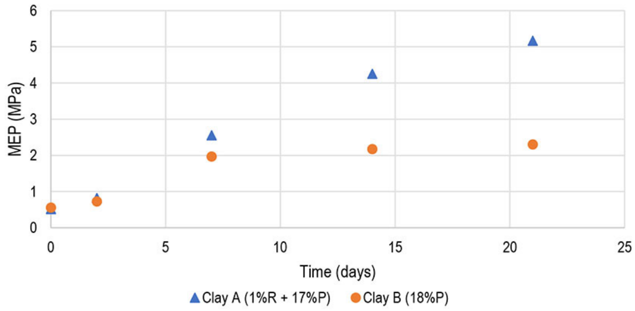

Figure 3—MEP of Clays A and B (R = resole resin; P = liquid pitch; Test temperature 35°C)

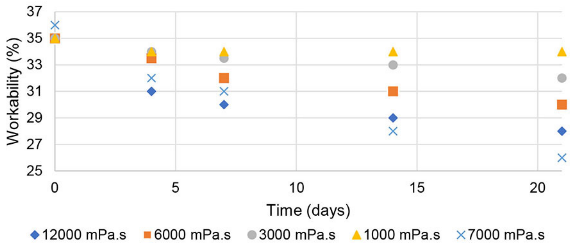

Figure 4—Workability ageing of Clay A at different binder viscosities

Properties of the aggregate and matrix raw materials

Wettability of the solid particles by polar and non-polar liquids

The wettability results for samples tested in both polar (water) and non-polar (hexane) media are shown in Figure 5. The gradients from Figure 5 for both hexane and water, as well as the calculated angles, are presented in Table 2. All calculated contact angles are less than 90°, indicating that all raw materials, both aggregate and matrix material, are wettable by water and are therefore considered to have polar surfaces. This implies that the system behaves as a homogenous viscoelastic suspension of aggregate and matrix materials within a pitch (and resin) medium. Consequently, segregation of filler material can be eliminated as a potential cause of increased viscosity.

Chemical compositions and mineralogy of the aggregate and matrix materials

The chemical compositions and mineralogy of the aggregates and matrix raw materials were determined using XRF, XRD, and SEM-EDS analyses. The calcined alumina was highly pure (>99 mass% Al_2O_3), with only a trace amount of Na_2O (0.14 mass%) as an impurity component. The andalusite had an alumina content of 62 mass%, with leucite ($KAlSi_2O_6$) as the main impurity. The bauxite contained 89 mass% Al_2O_3, with quartz and rutile (TiO_2) as the main impurities. The calcined clay contained corundum and cristobalite as main phases, with muscovite ($(KF)_2(Al_2O_3)_3(SiO_2)_6(H_2O)$) and rutile as impurity phases. The silicon carbide sample had a silicon carbide content greater than 90%.

The chemical composition and mineralogical analyses confirmed that none of the raw materials contained free lime or sulphur; components known to contribute to cross-linking of the binders used in taphole clay.

Characterisation of the liquid pitch, resole resin, and pitch-resin mixtures

The results reported in this section confirmed that there is an interaction between the resin and liquid pitch that not only alters the structure of the resin but also changes the viscosity of the resin-pitch mixture. These structural changes were investigated using FTIR, TGA, and DSC analyses.

Viscosity

The influence of shear rate on dynamic viscosity at 30°C was determined for the liquid pitch, resin, and resin-pitch combinations (Figure 6). The samples were tested after mixing and subsequent ageing at 45°C for two weeks. Shear rate tests revealed that both virgin resole resin and liquid pitch exhibit Newtonian behaviour. However, the age of resin-pitch mixtures displayed shear-thinning, non-Newtonian behaviour. The tendency of the zero-shear viscosity of the mixtures to exceed that of the virgin components clearly indicates an interaction between the resin and pitch. The extent of shear thinning increased with increasing resin content in the mixtures. This behaviour suggests a structural change wherein the polymer network of the resin breaks down into aggregate polymer chains or smaller polymer fragments (Gotro, 2018). The aged sample containing 75 mass% resole resin and 25 mass% liquid pitch could not be evaluated due to its excessively high viscosity.

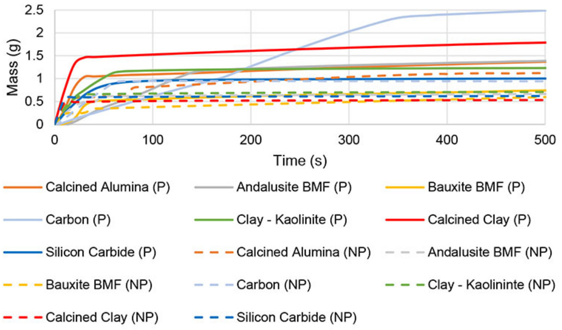

Figure 5—Wettability results for aggregate and matrix raw materials used in Clays A and B (P = polar medium, NP = non-polar medium)

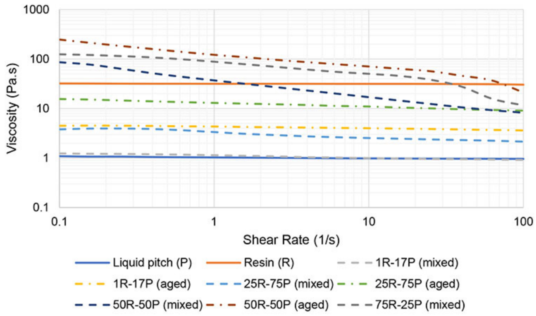

Figure 6—Shear rate vs. viscosity rheology test of liquid pitch (P), virgin resole resin (R) and combinations thereof after mixing and ageing at 45°C. (Tests conducted at 30°C)

The viscosity of the virgin binders and resin-pitch combinations as a function of temperature and time (for both mixed and aged samples) was evaluated after mixing and after ageing at 45°C for two weeks (Figure 7). The temperature range used for evaluation was 30°C–130°C to capture the gel point of the virgin resole resin

Table 2

Wettability constants and data used to calculate the contact angle between hexane (non-polar) / water (polar) and different aggregate and matrix materials

	Calcined alumina	Andalusite	Bauxite	Carbon	Clay - kaolin	Calcined clay	Silicon carbide
m^2/time (Hexane)	0.00574	0.00743	0.00286	0.02149	0.02117	0.00529	0.02985
m^2/t (Water)	0.00553	0.00675	0.00120	0.01751	0.00549	0.00520	0.01209
C_w	1.26E-07	1.63E-07	6.27E-08	4.71E-07	4.64E-07	1.16E-07	6.54E-07
θ	15.54	24.76	65.22	35.43	74.98	11.47	66.10

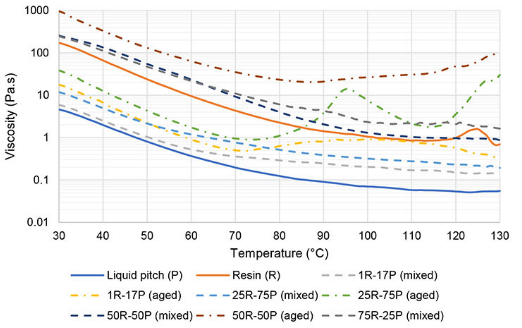

Figure 7—Changes in viscosity with an increase in temperature of resole resin, liquid pitch, and combinations thereof (shear rate = 1 sec^{-1})

at approximately 125°C. The viscosity of the virgin liquid pitch decreased with an increased temperature up to 110°C, after which it began to plateau. In contrast, the viscosity of the virgin resin decreased up to 118°C, followed by a sharp increase between 12°C and 126°C, consistent with the known curing region of resole resin (Wilmer, 2014; Gotro, 2014). Upon ageing, the samples exhibited an increase in initial viscosity, confirming that ageing contributes significantly to increased viscosity and, consequently, to reduced workability.

In the mixed (not aged) resin-pitch samples, no distinct increase in viscosity was observed within the 30°C–130°C range, unlike the virgin resole resin. This suggests that the presence of liquid pitch interferes with the resin structure required to initiate cross-linking, a typical behaviour in thermosetting resins (Fan, Weclawski, 2017). The viscosity of aged samples increased significantly, more so than that of the mixed samples, particularly in the 70°C–130°C range. As the resin content increased, the magnitude of the viscosity increase became more pronounced, presumably due to cross-linking starting at lower temperatures as a result of the higher reactive resin fraction.

The aged sample containing 25 mass% resole resin and 75 mass% liquid pitch exhibited multiple viscosity increases, one at 75°C–95°C and another between 115°C–130°C, which can be attributed to multiple curing reactions (Strzelec et al., 2012). This indicates that the onset of curing occurred at lower temperatures. Increasing the resin content also resulted in multiple curing reactions, some of which likely shifted to temperatures above 130°C.

Thermogravimetric analysis (TGA)

The rheological observations were supported by TGA, DSC, and FTIR analyses. TGA was used to evaluate the mass loss of the virgin resin and virgin liquid pitch samples in the temperature range of 30°C–130°C (Figure 8). The mass of both the resin and the pitch remained constant up to approximately 50°C. Beyond this temperature, the pitch began to exhibit mass loss, while the mass of the resin remained virtually unchanged up to 100°C. Above 100°C, a slight reduction in resin mass was observed, possibly due to the onset of water release associated with the gelation process. However, this minor mass loss is unlikely to significantly affect the viscosity changes observed in the pitch-resin mixtures used in the taphole clay.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) analyses were conducted from 20°C to 130°C in air, to simulate the reactions that occur during manufacturing (Figure 9). The peak at approximately 106°C for the virgin resole resin, corresponds to a mass loss at ~100°C observed in the TGA curve. The curing reaction occurred between 65°C–120°C and was marked by an exothermic peak (Haddadi et al., 2017).

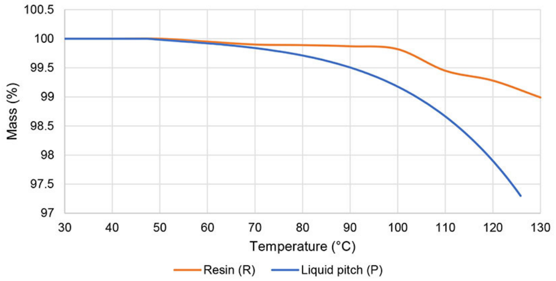

Figure 8—TGA analysis of virgin resole resin and liquid pitch binder (nitrogen atmosphere)

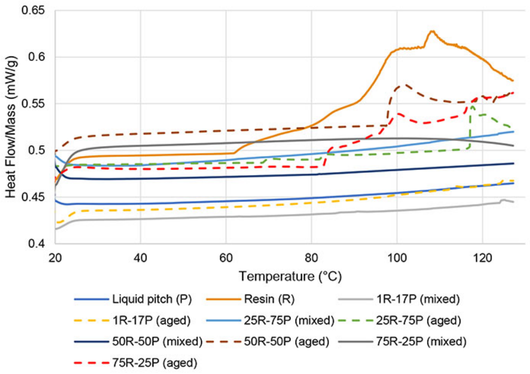

Figure 9—DSC results for liquid pitch, virgin resin, and resin-pitch combinations (mixed and aged in air)

The DSC curves of the virgin liquid pitch and the mixed resin-pitch combinations did not show any peaks during heating. This observation aligns with the viscosity results for the resin–pitch mixed samples, where no abrupt changes in viscosity were observed as the temperature increased. Both the DSC and viscosity data confirm that no curing reactions occurred in the resole resin-liquid pitch mixtures that were only mixed. This suggests that the structure of the resin is altered upon mixing with the liquid pitch, thereby preventing typical curing behaviour.

The aged resin-pitch mixtures however, exhibit distinctive exothermic peaks at various temperatures. As the proportion of resole resin in the mixtures increased, the exothermic peaks shifted to lower temperatures. By comparing these DSC results with the viscosity data of the aged resin-pitch samples, it is evident that curing of the resin-pitch mixtures occurs at lower temperatures than in the virgin resole resin. This is presumably due to a cross-linking interaction between the resole resin and the liquid pitch after mixing, which alters the structure of the resole resin. During ageing, the resole resin begins to cross-link prematurely.

Fourier-transform infrared spectroscopy – ageing and curing test

Fourier-transform infrared spectroscopy (FTIR) spectra of the liquid pitch, resole resin as well as the 1% resin – 17% pitch combination used in Clay A are shown in Figure 10. The spectrum of Clay A represents the unaged 1% resin – 17% pitch mixed. The identified functional groups are reported in Table 3. The structure of the resole resin was confirmed to be that of a phenol-formaldehyde structure (Authier-Matrin et al., 2001). Key features include a broad O-H peak at 3250 cm^{-1}, an SP2 C-H stretch at 3050 cm^{-1}, a cyclic aromatic structure peak at 1610 cm^{-1}, and C-O-C bonds between 1000 cm-1200 cm^{-1}.

Table 3

Interpretation of FTIR results for liquid pitch binder, resole resin, and resin-pitch combination used in Clay A

Observed wavelength (cm^{-1})	Wavelengths from literature (cm^{-1})	Functional groups
~3070	3000–3300	
~2900	2850–3000	N-H bond (R_2NH)
~1605	1600	SP3 C-H stretch
~1180	1180	C=C stretch (aromatic)
~750 (fingerprint)	750	C-N stretch
~730 (fingerprint)	737	Benzene C-H bending
Resole resin		N-H wag (R_2)
~3250	3200–3600	
~3050	3000–3150	O-H bonds (broad peak)
~2920	2850–3000	SP2 C-H stretch (hybridised) – peak overlaps with O-H
~1590	1600–1650	SP3 C-H stretch
~1200 (fingerprint)	1000–1200 (multiple peaks)	C=C stretch (aromatic)
~1033 (fingerprint)	1000–1200	C-O-C bonds

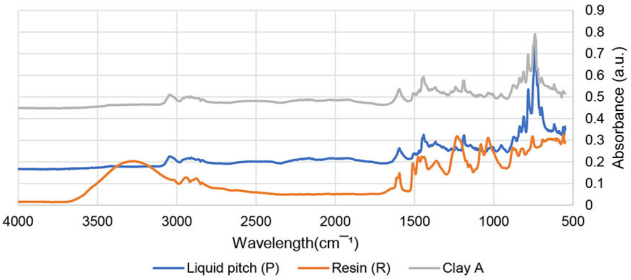

Figure 10—FTIR identification of functional groups associated with the liquid pitch, the resin, and resin-pitch mixture (1% resin – 17% pitch) used in Clay A (before ageing)

The FTIR spectrum of the liquid pitch in Figure 10 shows the presence of aromatics and SP C-H stretches. Due to the complex structure of the liquid pitch, overlapping peaks from various compounds are present. Distinctive functional groups such as secondary amines are identified by the N-H stretch (at ~3070cm^{-1}), C-N stretch (at ~1183cm^{-1}) and N-H wag (at 737cm^{-1}).

The spectrum of the resin-pitch mixture used in Clay A does not exhibit any major peak changes. It closely resembles that of the liquid pitch, with a minor change in the O-H bond region, which can be contributed to the presence of the resole resin in the sample.

To further investigate the effects of mixing, ageing and curing of the resole resin and liquid pitch, changes in viscosity and functional groups were evaluated using FTIR/ATR and DSC.

The possibility of early-onset cross-linking was evaluated through curing tests on the individual binders and corresponding FTIR analyses. The curing test involved heating the samples at 130°C for 2 hours to ensure complete curing. The result for the virgin resole resin is shown in Figure 11. During curing, free O-H bonds appeared at ~3680 cm^{-1} (Figure 11(a)), the SP3 C-H stretch at ~2920 cm^{-1} increased (Figure 11(b)), while the C-O-C stretch at ~1020 cm^{-1} increased significantly (Figure 11(c)), all of which indicate a higher cross-linking density during the curing process (Zhou et al., 2010).

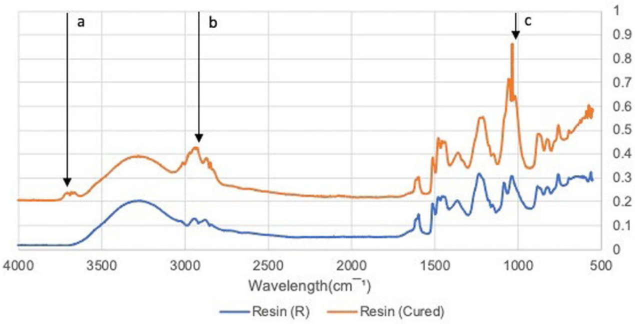

Figure 11—FTIR curve of virgin resole resin and resole resin cured at 130°C (a = free O-H bonds at ~3680 cm-1, b = SP3 C-H stretch at ~2920 cm^{-1}, c = C-O-C stretch at ~1020 cm^{-1})

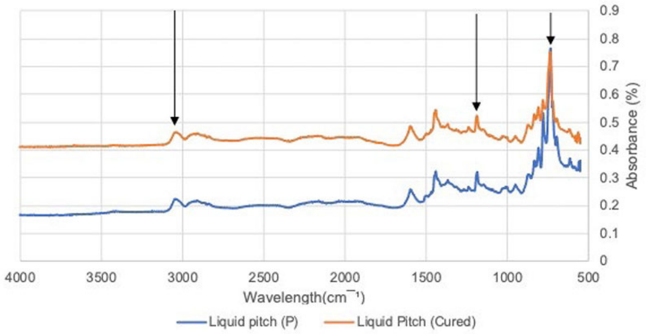

Figure 12—FTIR curve of virgin liquid pitch and liquid pitch cured at 130°C (arrows indicating the amine peaks)

The curing test result for the virgin liquid pitch is shown in Figure 12. As expected, no changes in functional groups were observed during curing, confirming the inertness of the virgin liquid pitch under the test conditions.

A second set of FTIR tests was conducted to identify functional group changes in samples that were mixed, aged, and cured. The mixed and aged test results correspond to the same samples used for viscosity and DSC analysis. The ageing and curing test results

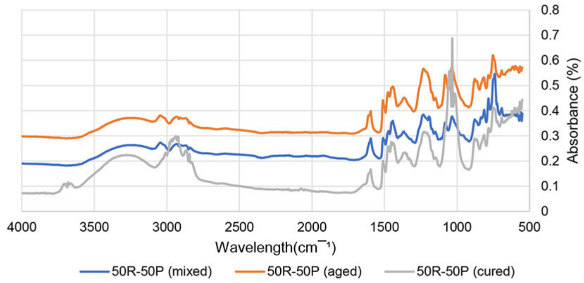

Figure 13—FTIR curves of 50 mass% resin-50 mass% pitch samples mixed, aged at 45 °C and cured at 130°C

for the 50 mass% resin – 50 mass% pitch mixture is given in Figure 13. A significant increase in the peak intensity of the C-O-C stretch functional groups at ~1020 cm^{-1} was observed. As the resin content increased, these C-O-C stretch functional group peaks in the aged samples also became more prominent. The increases in C-O-C functional group intensity between the mixed and aged samples is attributed to the cross-linking of the resole resin in the presence of liquid pitch (Anis et al., 2011; Dole, 1979).

There were no shifts in peak positions, only changes in the intensity of the C-O-C peaks. Peaks associated with secondary amines were present in the mixed, aged, and cured samples. In all three samples, the N–H peak at ~3070 cm^{-1} remained visible in the mixed and aged samples. In the cured sample, this peak was not easily identifiable due to overlap with a strong peak at 3000 cm^{-1}. However, its presence cannot be ruled out. The C-N stretch and N-H wag peaks, located at ~1180 cm^{-1} and ~737 cm^{-1}, respectively, were present in all three samples.

It is likely that the presence of secondary amines in the liquid pitch acts as a catalyst for the cross-linking of the resole resin during ageing, thereby accelerating the curing process. The FTIR results of the aged and cured samples confirm that, as the mixtures aged, the resin began to cross-link, resulting in an increase in the peak intensity of the C-O-C stretch functional group. This increase is most likely due to acetal ring formation, which is attributed to premature cross-linking of the resole resin catalysed by the secondary amines in the liquid pitch (Anis et al., 2011).

Conclusions

Causes for reduced workability and increased ageing of a blast furnace taphole clay were examined in this study. The following conclusions can be drawn:

- The workability of the investigated taphole clay decreased with time when 1% resole resin and 17% liquid pitch were used as binders, compared to using 18% liquid pitch alone. The reduction in workability was associated with an increase in binder viscosity.
- The MEP of the investigated taphole clay increased over time when resole resin and liquid pitch were used in combination, as opposed to using only liquid pitch.
- The surface chemistry of the aggregate and matrix raw materials was polar and compatible with that of the resole resin and liquid pitch used as binders. No impurities, such as sulphur or free lime, were detected in the aggregate or matrix raw materials that could have contributed to premature cross-linking of the resin.
- Mixtures of resin and pitch exhibited higher viscosities than either pure resin or pure liquid pitch and exhibited shear-thinning behaviour.
- The viscosities of resin-pitch mixtures increased with ageing due to premature cross-linking of the resin structure. C-O-C bonds between polymer chains became more prominent over time and with higher resin content. Functional groups of secondary amines were identified in the molecular structure of the liquid pitch.
- Premature cross-linking in the binder mixtures is likely caused by the secondary amines in the liquid pitch, which act as catalysts for the curing reaction of the resole resin. This, in turn, resulted in a lowering of the curing temperature of the resin-pitch mixtures.
- The observed reduction in workability of the taphole clay was therefore attributed to increased binder viscosity during ageing, caused by premature cross-linking in the binder system and the reduction in curing temperatures when resole resin was mixed with liquid pitch.

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Author credit statement

IJ-PC: Conceptualisation, investigation, writing original draft; SR: Supervision, writing - reviewing and editing of draft; AGC: Supervision, funding acquisition, Writing - reviewing and editing.

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