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Investigating the Use of Sugar Alcohol as an Alternative Non-Toxic Binder to Conventional Coal Tar/Coal Tar Pitch for Use in Taphole Clay

I. Cameron*, A. Garbers-Craig

Centre for Pyrometallurgy, Department of Materials Science and Metallurgical
Engineering, University of Pretoria, South Africa

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Abstract

Currently, the main purpose for obtaining alternative binders for use in taphole clay is to reduce the exposure to harmful polycyclic aromatic hydrocarbons (PAH) associated with conventional coal tar (CTht) binders. Some advances have been made such as using lower-PAH alternative binders or phenolic resole resins (resin-bonded) in taphole clays. The use of non-toxic binders has become exceedingly difficult due to the versatility of CTht in taphole clay. This study investigated a combination binder system that consisted of a sugar alcohol (research-grade glycerine) and phenolic resole resin as a potential non-toxic binder for use in platinum smelting taphole clay. The binder system was characterized according to its composition by means of Fourier-transform infrared spectroscopy and the PAH content (16-EPA-PAH) was determined using targeted gas chromatography mass spectroscopy. Flow behaviour of the binder was determined based on rotational rheology, and the volatilization and rheological thermal stability of the binders were assessed by means of thermogravimetric analysis and thermorheology, respectively. The effect of mixing these binder constituents on the cross-linking behaviour of the phenolic resin was evaluated using differential scanning calorimetry. The combination binder had a higher average mass loss and lower carbon yield compared to conventional CTht, but with a lower total PAH content, making it a more health-friendly alternative.

Keywords: Taphole clay, binder, PAH, non-toxic, sugar alcohol, resole resin.

I. Introduction

Taphole clays are granulo-viscoelastic materials consisting of oxide raw materials that make up the aggregates and part of the matrix, carbon raw materials in the form of coke or coal, powder plasticizers, high-temperature hardening additives, and binders [1]. The binder system conventionally used in taphole clay is one of three types: 1) pitch- or tar-bonded, 2) resin-bonded, or 3) a combination of pitch and resin. The pitch- or tar-bonded clays, also referred to as coal tar pitch-bonded clays, utilize pitch or tar from a coal source to serve as a binder at both room temperature and up to the sintering temperature of the oxide raw material [2,3]. The resin-bonded binder system utilizes a phenolic resin either as novolac or resole depending on the performance requirements. The novolac is generally cross-linked with compounds like hexa-methylene tetramine (HMTA) [4]. Because of the logistical difficulties with using the two-component system during manufacturing (preparation of the binder by mixing of the resin with the HMTA, followed by the curing process) and to ensure more accurate control over the curing of the resin, phenolic resole resin is conventionally preferred in taphole clays. The third type of binder system incorporates both the pitch/tar and resin [5] to assist with enhanced strength development of the clay. The phenolic resin supplies an increase in carbon yield [6] from the binder that assists with the high-temperature mechanical strength [7] of the taphole clay by providing a carbon network after heating of the clay.

Recently, significant emphasis has been placed on replacing pitch and tar binders in taphole clay with lower polycyclic aromatic hydrocarbon (PAH) binders to improve the health of persons working with these materials [2,8]. The exposure to PAH species is regulated by legislation in both the USA and EU as 16-EPA-PAH and 8-EU-PAH, respectively [2]. These protection agencies provide certain guidelines for the permissible exposure limits (PEL) within an 8-hour period, which in the case of the 16-EPA-PAH is $< 0.2\ \mathrm{mg/m^3}$ [6]. These guidelines give the total exposure limit in an 8-hour interval. Although standard laboratory practice does not simulate exposure for these extended periods, the total PAH of the binder needs to be considered. Along with the total PAH, the benzene equivalent (BE) is also used to describe and compare binders in order to get a holistic view of the total PAH content and its contribution to the toxicity of the clay [2]. In this study the 16-EPA-PAH is considered as the basis for evaluation

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* Corresponding author: izak.cameron@elkem.com

of PAH species in the binder, which is used to determine the toxicity (BE-value).

Some of the binders that have been investigated as lower PAH alternatives include phenolic resin [8], synthetic lower PAH pitch [3], petroleum-based pitches and synthetic oils [9]. The use of complex organic polymers, synthetic ethylene polymers, and diol/triol/polyol compounds has also gained interest with the aim of eliminating the PAH associated with the binder. For blast furnace applications, the binder system is usually a combination of phenolic resole resin and a secondary binder to improve the high-temperature mechanical properties, due to the lower carbon yield of some of the alternative binders. When heated, the phenolic resin condenses into o-methylol phenol and p-methylol phenol [10], and not benzene-linked species, which, as PAHs, are harmful carcinogens [8]. Even though this is the case, the inhalation of volatiles associated with phenol and formaldehyde is still a health concern and is also regulated in terms of permissible exposure. Resole resin is also sensitive to a change in temperature, which results in premature aging of the clay. This reduces the shelf-life of the clay and causes furnace instabilities like shorter tap-hole plugging lengths when these clays are used. The adhesion (drying ability) of the clay is largely dependent on the resin content, which in turn influences the taphole clay casting duration and tap-hole plugging length [11]. This creates some difficulties when this binder is used over extended periods.

The work presented in this paper investigated the use of a zero-PAH combination binder, consisting of sugar alcohol or glycerine, together with phenolic resole resin, in lieu of conventional coal tar (CTht) as binder in taphole clays. The focus of the paper is to describe the behaviour of the model binder (CTht) in terms of compositional, thermal, and mechanical properties, against which the sugar alcohol-phenolic resin mixtures are compared.

II. Materials and Methods

(1) Binders

The model taphole clay binder selected for evaluation in this study is from a coke-making process where the destructive distillation of coal produces a viscous liquid by-product called coal tar (CTht), also referred to as high-coking-value tar (HCVT), that is used as a binder for taphole clay. The mixtures that were tested as non-toxic alternatives were constituted of pure glycerine (research grade) and resole resin (gel time = 15 min at 130 °C, 4 500 cP at 25 °C). In the resole resin that was used, some of the phenol was substituted with lignin to lower the free phenol of the resin, which is a health concern, and to improve carbonization of the resin. The glycerine and phenolic resin mixture (Gly+PFR) was prepared by mixing glycerine and phenolic resin in a mass ratio of 1:5, using an overhead stirrer with impeller attachment rotating at 60 rpm and heated using a hot plate to 30 °C. The ratio of phenolic resin to glycerine is similar to what is used in practice and considered conservative values of resin addition. The second mixture (Gly+XG+PFR) consisted of glycerine that was plasticized with xanthan gum (XG) to increase the viscosity and mixed in the same mass ratio of 1:5 with phenolic resin (plasticized glycerine:PFR). The plasticizing of the glycerine was also done using an overhead stirrer with impeller attachment. The glycerine was heated to 60 °C on a hot plate and stirred for 30 minutes. After the glycerine had reached 60 °C, the xanthan gum was added in a mass ratio of 1:700 XG:Gly, stirring speed increased to 120 rpm and mixed for another 30 minutes. The mixture was allowed to cool to room temperature after which the resin was added and mixed again.

(2) Fourier-transform infrared spectroscopy

The liquid samples were analysed using a PerkinElmer Spectrum 100 spectrometer in attenuated total reflectance mode (UATR) to measure absorption at various wavelengths. The UATR accessory consisted of a diamond-Zn/Se measuring system. Data capturing was done using Spectrum 10 software. A background scan was performed to remove noise from the spectrums. A CO_2 and H_2O filter was used to remove peaks associated with these species from the samples. The analysis was conducted between wavelengths 600 – 4 000 cm^{-1} with a total of 32 scans per sample.

(3) Gas chromatography mass spectroscopy (targeted)

The model binder and the mixture of glycerine and resole resin were analysed by means of gas chromatography mass spectroscopy (GC-MS) in targeted analysis to determine the quantity of 16-EPA-PAH species in the volatiles of each sample. The samples were constituted in toluene or hexane similar to what is described by earlier works by Cameron *et al.*, 2024 [11]. The CTht was constituted in toluene and the glycerine mixtures in hexane. Before the binders were analysed, a pesticide standard (Merck polynuclear aromatic hydrocarbons 16 solution) containing the 16-EPA-PAH species was used to construct a calibration curve by analysing both dilute and concentrated solutions of the standard. This facilitated the process of determining the quantity of each of the 16-EPA-PAH species in the binders.

(4) Thermogravimetric analysis

The degree of mass loss of the binders were determined by examining their thermal stability and volatilization behaviour. Samples were heated in a Hitachi STA 7300 TGA, utilizing TA 700 software for measuring and data capturing. The liquids, weighing between 5 and 10 mg, were placed in 30-μL alumina crucibles. The TGA furnace was purged with nitrogen at 20 mL/min to maintain an inert heating environment, after which the samples were heated from 50 °C to 800 °C at a heating rate of 10 K/min. The STA 7300 setup also enables DTA analysis with differential scanning calorimetry (DSC). The residual material remaining in the crucible after heating was reported as the carbon yield, i.e. material remaining after carbonization. For each liquid binder, three samples were tested. An average volatile loss is reported for each sample.

(5) Differential scanning calorimetry

The changes in exothermic peaks due to possible reactions resulting from mixing the resole resin with the glycerine were investigated. This was done to identify whether there is a change in the gelation (cross-linking) temperature range of the resole resin when mixed with other binders as this has been shown to be problematic if early onset of gelation occurs that results in pre-mature ageing of the taphole clay [12]. The volatilization temperatures of the binders were also identified based on endothermic peak identification. Samples of the binders, weighing between 5 and 8 mg, were placed in 30-µL aluminium crucibles and sealed with alumina lids. An empty sealed crucible with a pan was used to calibrate the DSC and a background was run to remove these peaks from the binder sample peak identification. Samples were heated at 5 K/min up to 300 °C and purged with nitrogen at 20 mL/min to maintain an inert heating environment.

(6) Rheology

The rheology evaluation of the binders was performed using two different tests, both at a constant shear rate of 1 sec^{-1}: 1) isothermal rotational test at 45 °C, and 2) test on the change in dynamic viscosity (rotation) as a function of temperature (temperature sweep) from 30 °C to 150 °C. The rheometer that was used for evaluation of the samples was an Anton Paar Physica MCR 501 with a cone-plate configuration and Peltier PTD 200 temperature control system to heat the samples during evaluation. RheoCompass^{TM} software was used to program the rheometer and capture the test data. The experimental setup for the isothermal rotational test involved shearing between 0.1 – 100 sec^{-1}. For the temperature sweep, the shear rate was selected as 1 sec^{-1} and samples were heated at 5 K/min whilst measurements were taken at each temperature. Three replicates of each test were conducted, and the closest corresponding values between the isothermal rotational test and the temperature sweep were recorded.

III. Results and Discussion

(1) Compositional analysis

This section describes the functional groups present in each binder and the raw materials, such as plasticized xanthan gum and resole resin, whereby the molecular structures of the pure raw materials and of the mixtures could be identified, using FTIR. It also reports on the presence and content of 16-EPA-PAH species in each binder, as determined by means of GC-MS targeted analysis.

(a) *Fourier-transform infrared spectroscopy analysis*

The FTIR spectrum of the reference binder used in taphole clay (CTht) is shown in Fig. 1. The spectrum shows the major functional groups that were identified for this binder. The functional groups that were selected for interpretation occurred mainly in the wavelength range of 1 400 – 3 600 cm^{-1}. Wavelengths below 1 400 cm^{-1} were taken into consideration, based on the overall main functional groups identified, if distinctive peaks were observed in this area. The CTht peaks that were identified occurred at 1 444 cm^{-1} and 1 592 cm^{-1} correspond to C=C stretches, which indicates the presence of cyclic aromatic hydrocarbons. The distinctive peak at 3 040 cm^{-1} corresponds to an alkylated sp^2-hybridized C-H stretch, which, along with the C=C functional groups, indicates the presence of benzene molecules [2]. The co-eluted C=O peak at 1 643 cm^{-1} confirms the presence of some carbonyl functional groups. The fingerprint area (< 1 400 cm^{-1}) also reveals peaks at 1 236 cm^{-1} and 1 185 cm^{-1}, which are due to C-O-C bonds, generally present in cross-linked polymers. This suggests partial polymerization of the pitch.

The individual raw materials, i.e., pure glycerine, plasticized xanthan gum, and phenolic resole resin were also evaluated. The FTIR spectrum of pure glycerine is shown in Fig. 2, highlighting the identified peaks and corresponding functional groups. The glycerine used for investigation is from a pure source, as confirmed by the absence of the crude glycerine peaks in the spectrum [13]. The broad peak at 3 271 cm^{-1} corresponds to O-H stretch associated with alcohols. Peaks of sp^3-hybridized C-H stretching are detected at 2 870 cm^{-1} and 2 920 cm^{-1}. The co-eluted peaks at 1 400 – 1 420 cm^{-1} are due to C-O-H bending and C-O stretching (1 112 cm^{-1}), which are indicative or primary alcohols [13].

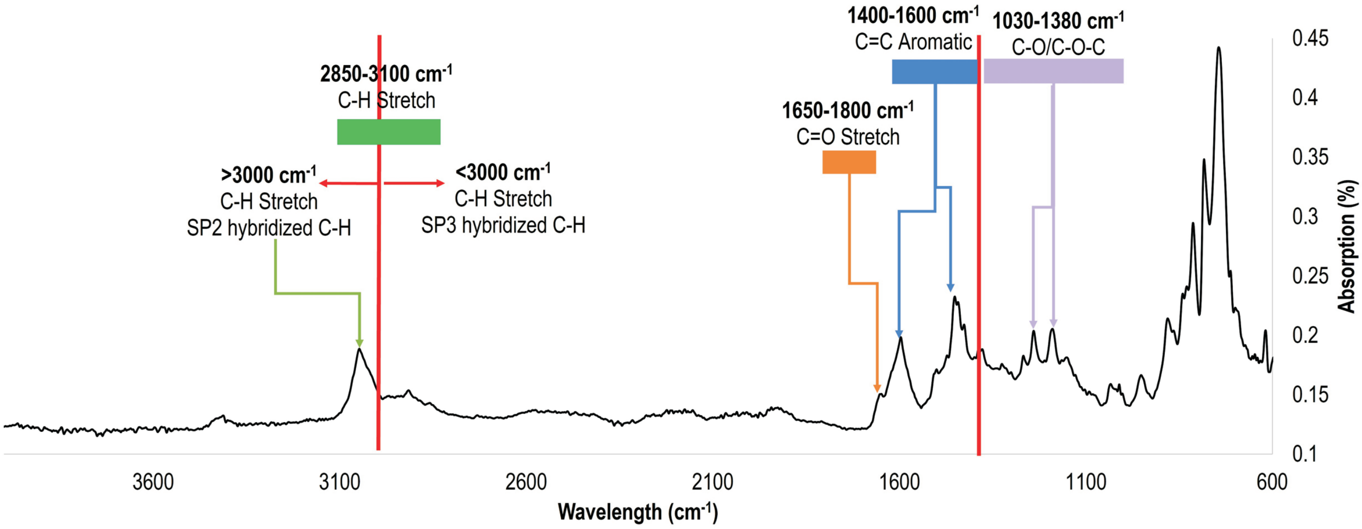

Fig. 1: FTIR spectrum of CTht highlighting the main functional groups.

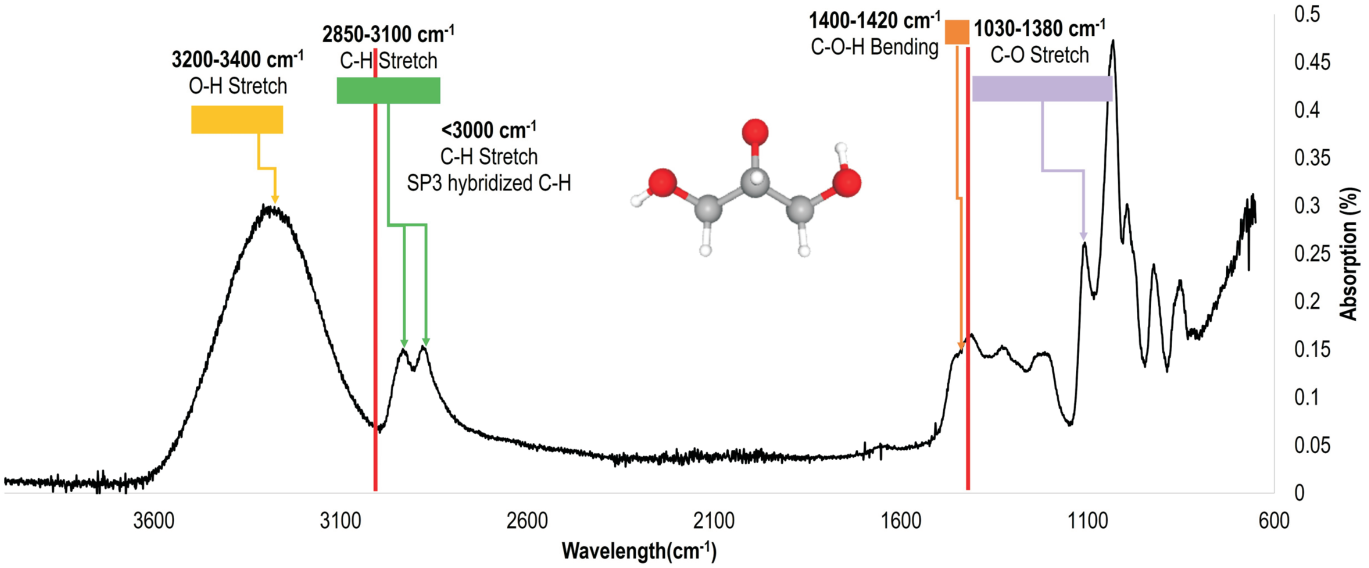

Fig. 2: FTIR spectrum of pure glycerine highlighting the main functional groups.

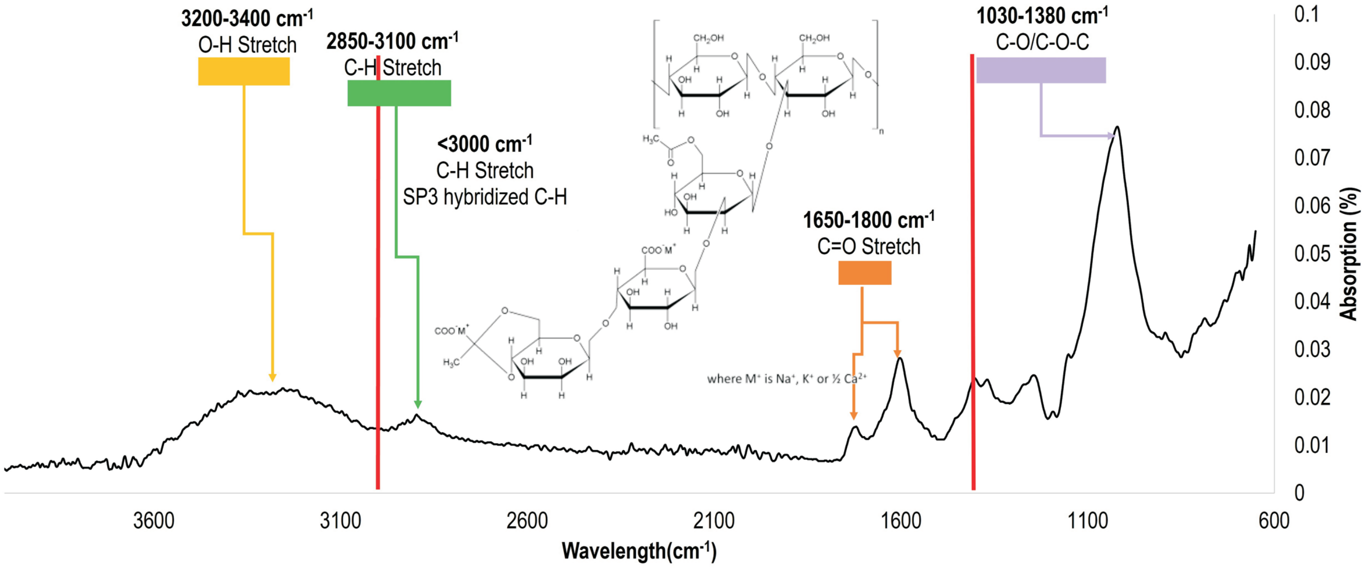

Fig. 3: FTIR spectrum of xanthan gum highlighting the main functional groups.

A powdered plasticizer was used to adjust the viscosity of the glycerine before it was mixed with the resole resin. The plasticizer used was xanthan gum from *xanthomonas campestris,* of which the FTIR spectrum with identified peaks is shown in Fig. 3. The xanthan gum is an anionic polysaccharide polymer with a branched molecular structure. The xanthan gum shows a less distinctive O-H stretching peak at 3 295 cm^{-1}. Similar to the pure glycerine, there were also sp^3-hybridized C-H stretches present but to a lesser extent. The C=O stretching vibration of acetate was attributed to the peaks at 1 650 cm^{-1} and 1 700 cm^{-1} and the lower absorption of C-O-O peak at 1 400 cm^{-1}. The distinctive peak at 1 020 cm^{-1} was assigned to the C-O acetate stretch [14]. The presence of O-H functional groups in glycerine makes it a favourable plasticizer for xanthan gum and ensures a polarity match between glycerine and phenolic resole resin to aid proper mixing and stability of the mixture.

The second raw material for the mixtures is the phenolic resole resin of which the FTIR spectrum with identified functional groups is shown in Fig. 4. Similar to pure glycerine and xanthan gum, an O-H stretch peak corresponding to an alcohol functional group is observed at 3 270 cm^{-1}. This O-H stretch is present in the C-OH structure [15], which could be due to the carrier material used for the phenolic resin. The presence of sp^3-hybridized C-H stretches at 2 925 cm^{-1} and 2 870 cm^{-1} indicated an aliphatic structure (methylene functional groups) present in the phenolic structure situated between the aromatic rings [15]. The resin contained a small amount of residual formaldehyde, identified by the low absorption peak at 1 645 cm^{-1} that is related to a C=O carbonyl double bond [15]. The C=C vibration at 1 400 – 1 600 cm^{-1} occurs between the aromatic rings in the resin structure. The possibility of sp^2-hybridized C-H stretching could also be present in the sample, with co-elution of the peaks occurring above 3 000 cm^{-1}, overlapping with the O-H stretch.

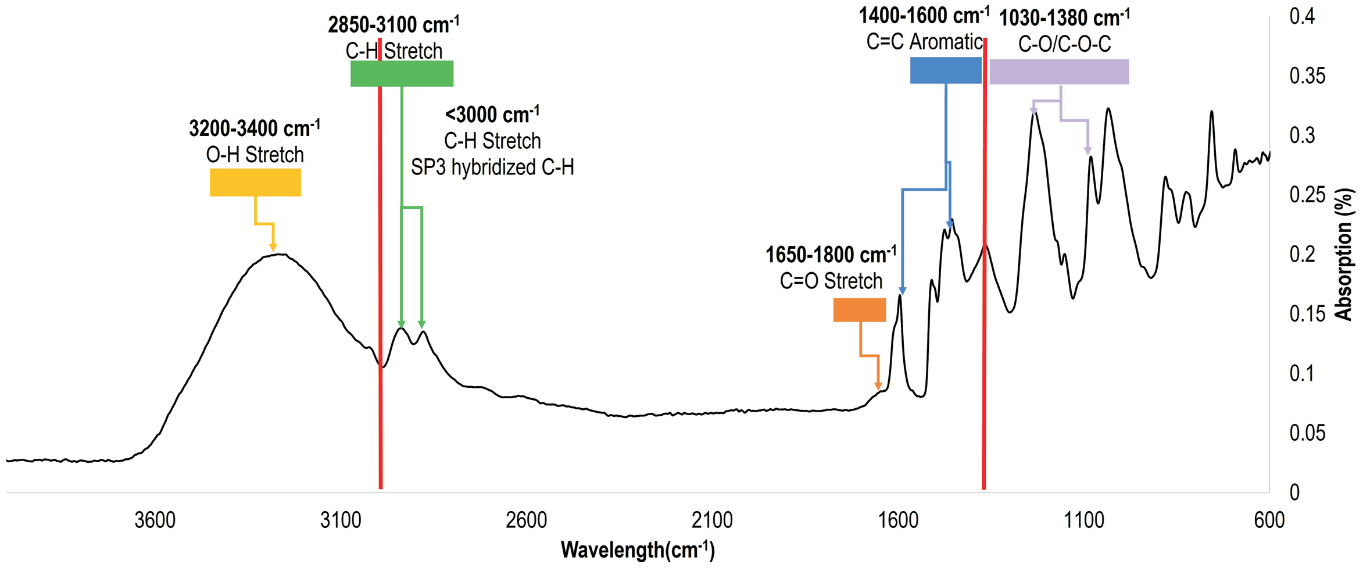

Fig. 4: FTIR spectrum of resole resin highlighting the main functional groups.

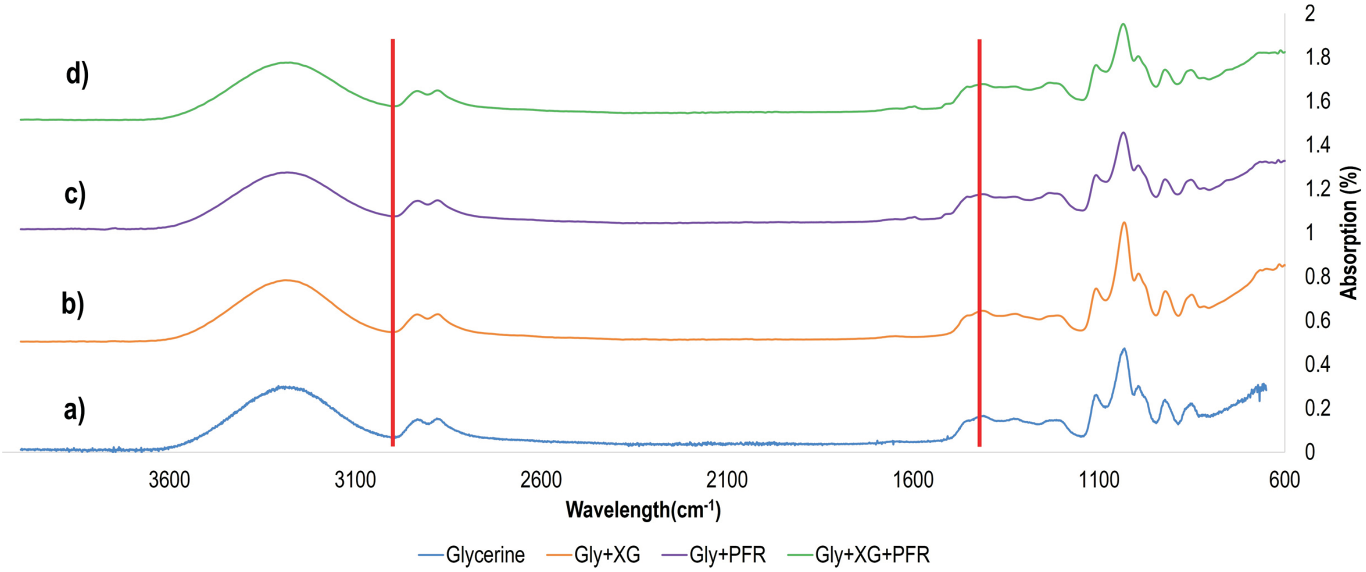

Fig. 5: FTIR spectra showing identified functional groups for a) pure glycerine, b) glycerine plasticized with xanthan gum, c) glycerine and resole resin mixture, and d) glycerine-plasticized xanthan gum mixed with resole resin.

The two peaks identified in the C-O/C-O-C region are described as vibrations of alkyl phenol (at 1 220 cm^{-1}) and deformation vibration of C-H in aromatic rings (at 1 080 cm^{-1}) [15].

The FTIR spectra of the two alternative binders being investigated for taphole clay use (mixtures Gly+PFR and Gly+XG+PFR) are shown in Fig. 5. Also included in Fig. 5 are the FTIR spectra of pure glycerine and the plasticized glycerine. The peaks identified showed that irrespective of whether the glycerine was plasticized or mixed with phenolic resole resin, the molecular structure of the binder system remained the same as that of pure glycerine. The distinctive peaks for the xanthan gum and resole resin were not identified in the samples due to the small quantity that was added [12]. The structures of all the mixtures remain aliphatic. The aliphatic nature of these binders will not yield the same degree of carbonization and would not volatilize in a similar manner to the conventional tar binder used in taphole clay. The volatilization behaviour and residual carbon after firing of these mixtures were therefore evaluated.

(b) *Gas chromatography mass spectroscopy (targeted) analysis*

The second compositional investigation consisted of determining the toxicity of the binders. GC-MS was used to determine the content of the 16-EPA-PAH in each of the binders. The results were used to calculate a toxicity coefficient (BE-value) as shown in Equation 1 [16].

$$\begin{aligned} BE &= 1.00C_{BaP} \\ &+ 0.034C_F + 0.033C_{BaA} + 0.26C_C + 0.10C_{BbF} \\ &+ 0.05C_{BeP} + 0.10C_{IP} + 1.40C_{DBA} + 1.00C_{BP} \end{aligned} \tag{1}$$

Where C_{BaP} is the mass% benzo(a)pyrene, C_F is the fluoranthene content, C_{BaA} is the benzo(a)anthracene content, C_C is chrysene, C_{BbF} is benzo(b)fluoranthene content, C_{BeP} is benzo(e)pyrene content, C_{IP} is the indeno(1,2,3-cd)pyrene content, C_{DBA} is dibenzo(a,h)anthracene, and C_{BP} is the content of benzo(g,h,i)perylene.

Although the calculation of the BE-value provides a good approximation for characterizing the toxicity of the binders, an additional measure was included because the majority of the binders investigated in this study were aliphatic. The content of each 16-EPA-PAH and permissible exposure limit were reported, allowing for comparison of the alternative binders with the reference binder. The GC-MS targeted analysis results are shown in Table 1. The targeted analyses of pure glycerine (Gly) and Gly+XG were identical, with no 16-EPA-PAH species detected. The values of the identified PAH species were similar for the Gly+PFR and Gly+XG+PFR mixtures. The concentrations in Table 1 are given in parts per million (ppm) to allow comparison with the permissible exposure limits (PEL) of each PAH species. The PEL-values given in Table 1 are based on 8- or 10-hours exposure times. Since the gasification period of the sample in the GC-MS is shorter than the PEL exposure time, the values of the 16-EPA-PAH serve only as guidelines to determine which of the binders would be more or less challenging (relative comparison) to comply with the prescribed exposure limits for each species.

The toxicity of the reference binder (CTht) is 1.65, which falls within the range of PAH content reported in the literature for fluid coal tars [16]. As previously mentioned, and shown in Table 1, the glycerine-based binders have a BE value of zero, indicating zero toxicity. However, in the comparison of the values of each 16-EPA-PAH, some of the species exceed the PEL, even with the short gasification period in the GC-MS. This means that at longer exposure times, the binder would still be considered toxic.

Pure glycerine did not show any aromatic structures in the FTIR results, whereas the resole resin did contain an aromatic structure. The results in Table 1 show that, for this specific resin, a few 16-EPA-PAH species exceeded the PEL, indicating a risk for long-term exposure (8 – 10 h). The mixtures of glycerine and phenolic resole had lower levels of certain PAH species, however, they were still above the PEL. These results indicate that, regardless of the primary binder selected as non-toxic alternative for the taphole clay, the presence and quantity of PAH species in the resole resin determine the overall toxicity. Current alternative approaches, such as replacing phenol and formaldehyde with non-toxic alternatives such as lignin and furfural, can, to some extent, help address this challenge [23, 24].

(2) Thermogravimetric analysis

The high-temperature stability and volatilization of the binders were investigated using thermogravimetric analysis. The inflections points on the TG curves were plotted as a cumulative mass loss, referred to as average mass

Table 1: Targeted GC-MS analysis of binders showing 16-EPA-PAH species, calculated benzene equivalent, and permissible exposure limits (PEL) [17, 18, 19, 20, 21, 22].

Compound	Boiling point (°C)	Formula	PEL (ppm)	CTht (ppm)	PFR (ppm)	Gly+PFR (ppm)	Gly+XG+PFR (ppm)
Naphthalene	218	$C_{10}H_8$	0.1 (8 h)	37 667	354	12	12
Acenaphthylene	270	$C_{12}H_8$	**	9 480	122	-	-
Acenaphthene	279	$C_{12}H_{10}$	0.03 (8 h)	531	5	4	4
Fluorene	295	$C_{13}H_{10}$	0.1 (10 h)	8162	16	-	-
Phenanthrene	338	$C_{14}H_{10}$	0.03 (8 h)	20 430	19	-	-
Anthracene	340	$C_{14}H_{10}$	0.03 (8 h)	6 270	28	1	1
Fluoranthene	383	$C_{16}H_{10}$	**	12 971	45	1	1
Pyrene	393	$C_{16}H_{10}$	0.025 (8 h)	7 560	31	1	1
Chrysene	441	$C_{18}H_{12}$	0.02 (8 h)	8 773	5	-	-
Benzo(a)anthracene	435	$C_{18}H_{12}$	0.02 (8 h)	3 757	12	-	-
Benzo(b)fluoranthene	481	$C_{20}H_{12}$	0.01 (10 h)	8 777	1	-	-
Benzo(k)fluoranthene	481	$C_{20}H_{12}$	0.02 (8 h)	151	2	-	-
Benzo(a)pyrene	496	$C_{20}H_{12}$	0.02 (8 h)	5 132	1	-	-
Indeno(1,2,3-cd)pyrene	524	$C_{22}H_{12}$	0.02 (8 h)	2 741	1	-	-
Dibenzo(a,h)anthracene	539	$C_{22}H_{14}$	**	1 301	0.1	-	-
Benzo(ghi)perylene	545	$C_{22}H_{12}$	**	2 316	0.2	-	-
BE			-	1.65	0.00	0.00	0.00

** no defined PEL for these compounds

loss (g/K), from the point at which the samples started to volatilize up to 800 °C. The average mass loss of the glycerine-based binders is shown in Fig. 6 and provided in Table 2. The average mass loss as well as the volatilization temperature ranges are also given in Table 2.

The average mass loss of the glycerine-based binders is nearly an order of magnitude higher than that of the reference binder (0.28 vs. 1.57 – 1.79 g/K). The temperature range over which the glycerine-containing binders volatilized was from 50 °C to approximately 230 – 240 °C, which is over 30 % smaller than the range for the reference binder (70.8 – 380 °C). This means that the reference binder volatilizes to a lesser extent over a broader temperature range. This is presumably due to the large variety of PAH species with complex aromatic compositions in the reference binder, which volatilize at different temperatures. This lower degree of volatile loss over a wider temperature range results in less porosity in a CTht-bonded THC and reduces the risk of crack damage from the sudden release of a large amount of volatiles.

Given that the condensation reaction of the tar/pitch used in taphole clay carbonizes and transforms into a carbon network that contributes to high-temperature mechanical strength, the carbon yield of the binders was also determined from the TGA analysis. The carbon yields of the starting raw materials and phenolic resole resin used in the glycerine-mixtures, as well as the binders themselves, are shown in Fig. 7. Tar has a higher carbon yield than glycerine, as pure glycerine does not carbonize. This highlights the challenge of using glycerine-containing binders in taphole clay, as they do not contribute additional strength to the THC when heated. For this reason, phenolic resin should be included in a mixture due to its higher carbon yield, which enhances the overall strength of the binder. The addition of resole resin to glycerine in a 1:5 Gly to PFR mass ratio results in a 2.8% increase in carbon yield when using this specific resin composition. Similarly, the addition of resole resin to the plasticized mixture resulted in a similar carbon yield (2.5 %). The plasticizing agent contributes a 24.7 % carbon yield, but given the small amount used, its impact on the overall carbon yield of the binder is insignificant compared to the contribution of the resole resin.

Even though the carbon yield of the glycerine mixtures is lower than that of the reference binder, these values represent improvements over the zero-carbon yield of pure glycerine. The importance of having a binder with a low average mass loss spread across a wide temperature range is that it ensures the formation of finely distributed internal pores in the matrix of the taphole clay and provides sufficient strength. The low average mass loss also helps prevent taphole turbulence or blowout when taphole clay is extruded through the tapping channel and comes in contact with molten material inside the furnace [9].

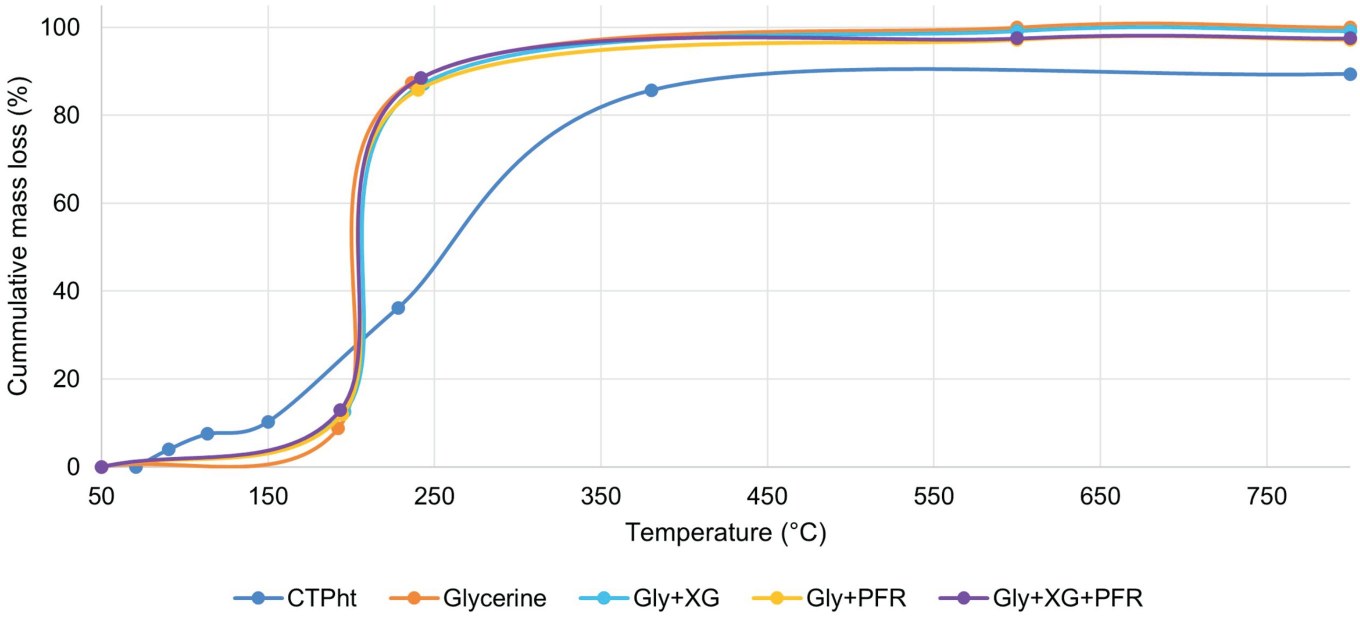

Fig. 6: Inflection points and cumulative mass loss of glycerine-based binders and CTht between 50 – 800 °C.

Table 2: Summary of inflection points and average mass loss over volatilization temperature range.

Binder	Inflection point temperature (°C)	Average mass loss over temperature range (g/K)	Temperature range, ΔT (K)
CTht	70.8; 90.5; 113.5; 150.1; 228.2; 380.4	0.28	70.8 – 380.4 (ΔT ~ 310)
Glycerine, Gly+XG, Gly+PFR, Gly+XG+PFR	~193; ~242; ~600	1.57 – 1.79	50.0 – 240 (ΔT ~ 190)

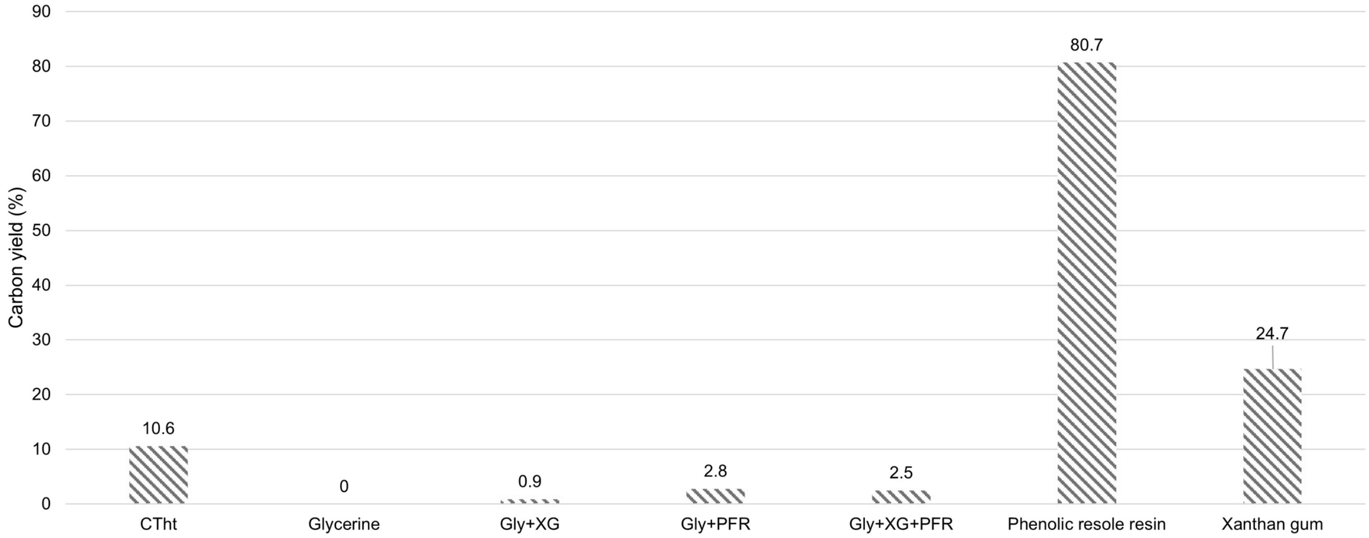

Fig. 7: Summary of carbon yield of binders heated to 800 °C in nitrogen.

(3) *Differential scanning calorimetry analysis*

For this study, the concept of using glycerine as an extender for the phenolic resole resin was the premise. Additionally, plasticizing the glycerine with xanthan gum to increase the viscosity for clay mixing was another measure to be investigated. Because both xanthan gum and resole resin were mixed with the glycerine, it was important to understand how this would influence the curing temperature range of the resin. As shown in previous work, mixing phenolic resole resin can alter the molecular structure and composition, either increasing or decreasing the curing temperature [12]. To explore this, the exothermic and endothermic peaks associated with reactions such as crosslinking, polymerization and volatilization of the binders were investigated. Fig. 8 shows the DSC results with endo- and exothermic peaks of each binder. The reference binder results are not reported as no noticeable exothermic peaks were identified at temperatures below 150 °C, although some volatilization endothermic peaks were observed.

The pure glycerine did not show any peaks until 221 °C, after which a series of endothermic peaks appeared up to 270 °C. These peaks can be correlated to the volatilization of low-temperature aliphatic hydrocarbons in the binder, based on the TGA results. The constant heat flow below 150 °C for this binder indicates that no low-temperature volatiles, such as potential moisture, were detected. The resole resin also showed no low-temperature volatiles. Two distinctive exothermic peaks were identified at 159.6 °C and 163.0 °C, both associated with the polymerization of the phenolic resin during curing. The first peak at 159.6 °C could be attributed to one of two processes: 1) dehydration condensation of hydrocarbons, 2) start of polymerization [25]. The second peak at 163.0 °C indicates the final curing of the resin, facilitated by the cross-linking of the monomer chains [25]. Both these processes occur during the curing of phenolic resin and are necessary to ensure the final set of the resin during heating. The desired curing temperature range for the resin is below 200 °C, allowing it to start developing strength before the pitch or tar starts to coalesce and form meso-phase as heat is increased in conventional binders for taphole clay.

For the glycerine-phenolic resin binders, some exothermic peaks were identified close to the same temperature as those in the pure resole resin. Plasticizing the glycerine did not significantly alter the endothermic volatilization behaviour compared to pure glycerine. When mixing resole resin with glycerine (Gly+PFR), only one peak was observed at 182.4 °C. Due to the quantity of resin in the mixture, the first exothermic peak identified in the pure resole resin could not be detected. The peak identified at 182.4 °C is attributed to the gelation reaction of the binder. This reaction generates a more exothermic response compared to the final curing, which is why the peak is attributed to gelation of the resin in the mixture. An observation was that the peaks identified in the glycerine-based binders shifted to higher temperatures as compared to the pure resole resin peak at 163.0 °C. The mixing of glycerine with phenolic resole resin resulted in a shift towards a higher gelation temperature. Additionally, the mixing of the phenolic resole resin with the glycerine resulted in a more thermally stable molecular structure, as indicated by the endothermic peaks observed at higher temperatures than those in the pure glycerine binder.

The plasticized resin mixture (Gly+XG+PFR) exhibited different thermal behaviour compared to both glycerine and phenolic resole resin. An exothermic peak at 193.7 °C is attributed to the gelation of the resin in the mixture. At higher temperatures, a series of endothermic peaks between 220–270 °C is observed, corresponding to the volatilization of glycerine in the binder. The gelation of this binder occurs approximately 30 °C higher than that of the pure resole resin, moving the gelation temperature closer to the 200 °C mark, which is important for clay strength development. The Gly+PFR binder shows the most favourable thermal behaviour, with the smallest shift in gelation temperature compared to the pure resin.

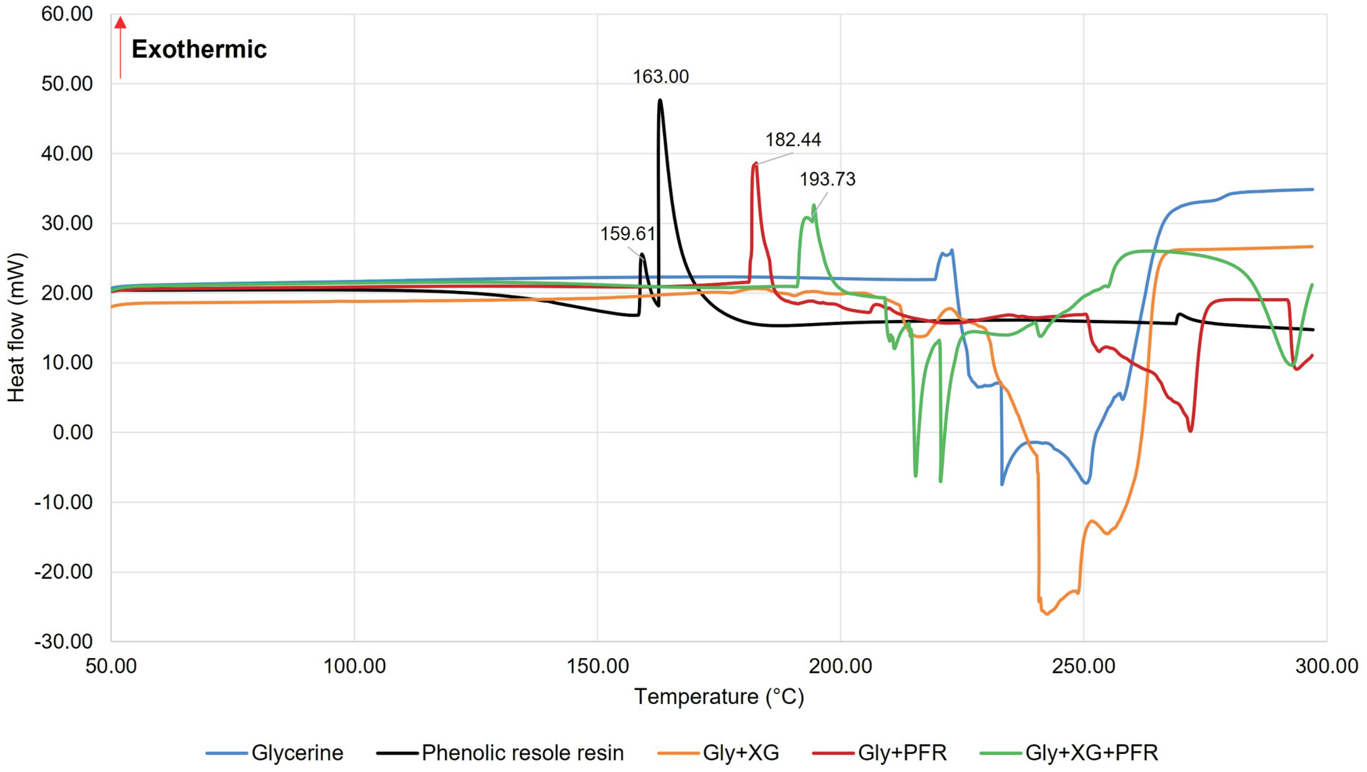

Fig. 8: Endo- and exothermic heat flow peaks of various binders.

(4) Rheology

This section describes the behaviour of the model binder (CTht) used in taphole clay according to its flow properties (viscosity as a function of shear rate) and thermal stability (viscosity as a function of temperature up to 150 °C). The alternative binders were also evaluated and compared to the characteristic behaviour of the model binder.

(a) *Glycerine- and polymer-based binders*

The Newtonian behaviour of the binders, characterized by viscosity as a function of shear rate in rotation, tested at 45 °C, is shown in Fig. 9. The test temperature of 45 °C was selected as the optimal mixing temperature for taphole clay following binder addition to ensure homogeneous mixing of the clay.

The results indicate a combination of Newtonian and non-Newtonian (shear-thinning) behaviour. The viscosity of the reference binder remained relatively constant, with an initial viscosity of 0.40 Pa·s. The viscosity remained constant with an increase in shear rate, indicating the Newtonian behaviour of the liquid. The pure glycerine had a lower viscosity than the reference binder, starting at 0.27 Pa·s. Although the binder exhibited shear-thinning at shear rates below 1.0 s^{-1}, the behaviour remained Newtonian with a constant viscosity across the remaining shear rate range. The use of pure glycerine as a binder in taphole clay would be advantageous as it would reduce the quantity of binder needed for clay mixing, shorten the ageing time of the clay and lower extrusion pressure during mud gun operations for extruding the clay into the tap hole. However, the lower viscosity and viscoelasticity of the binder could lead to problems in functionality as a binder for taphole clays, due to reduced plasticity of the clay.

Plasticizing of the glycerine with xanthan gum increased the viscosity by an order of magnitude compared to both the reference and pure glycerine values. This plasticization of the glycerine produced a molecular structure that is less resistant to shear deformation, as shown by the non-Newtonian, shear-thinning behaviour of the binder. The plasticization of the biopolymer with glycerine weakened the strong hydrogen bonding of the molecular structure, resulting in a structure that is less resistant to deformation than pure glycerine. Combining a higher viscosity with shear-thinning behaviour can improve the extrusion of the taphole clay if such a binder is used [26]. The addition of phenolic resin to the plasticized mixture (Gly+XG+PFR) did not significantly alter the molecular structure, as no noticeable change in the viscosity or Newtonian behaviour of the binder was observed.

The addition of phenolic resin to the reference binder (CTht+PFR) resulted in a greater increase in viscosity (1.25 Pa·s) as compared to the glycerine version (0.4 Pa·s). Mixing phenolic resin with tar also produced a molecular structure that is less resistant to deformation than the pitch itself, exhibiting non-Newtonian, shear-thinning behaviour. This binder is conventionally used in most taphole clays, particularly for high-throughput blast furnaces. When the phenolic resin is mixed with pure glycerine, a different behaviour is observed, where the mixture exhibits Newtonian behaviour. This was considered as a direct substitution for tar and phenolic resole resin in taphole clay as part of this study. The glycerine-resin mixture had an initial viscosity in the same range as the pure glycerine, with only a slight increase in viscosity due to the addition of the higher viscosity resin. The preservation of the Newtonian behaviour in the glycerine-resin mixture could be attributed to the formation of a molecular

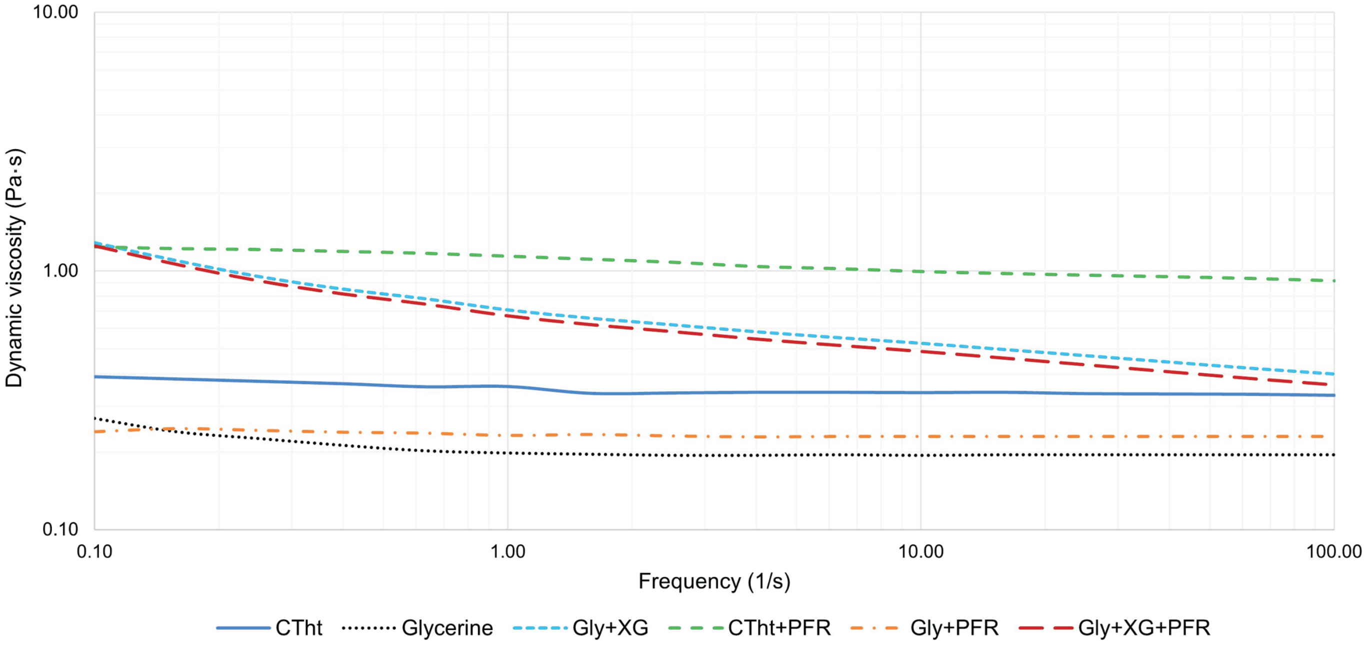

Fig. 9: Change in dynamic viscosity as a function of shear rate (Newtonian behaviour) of various binders.

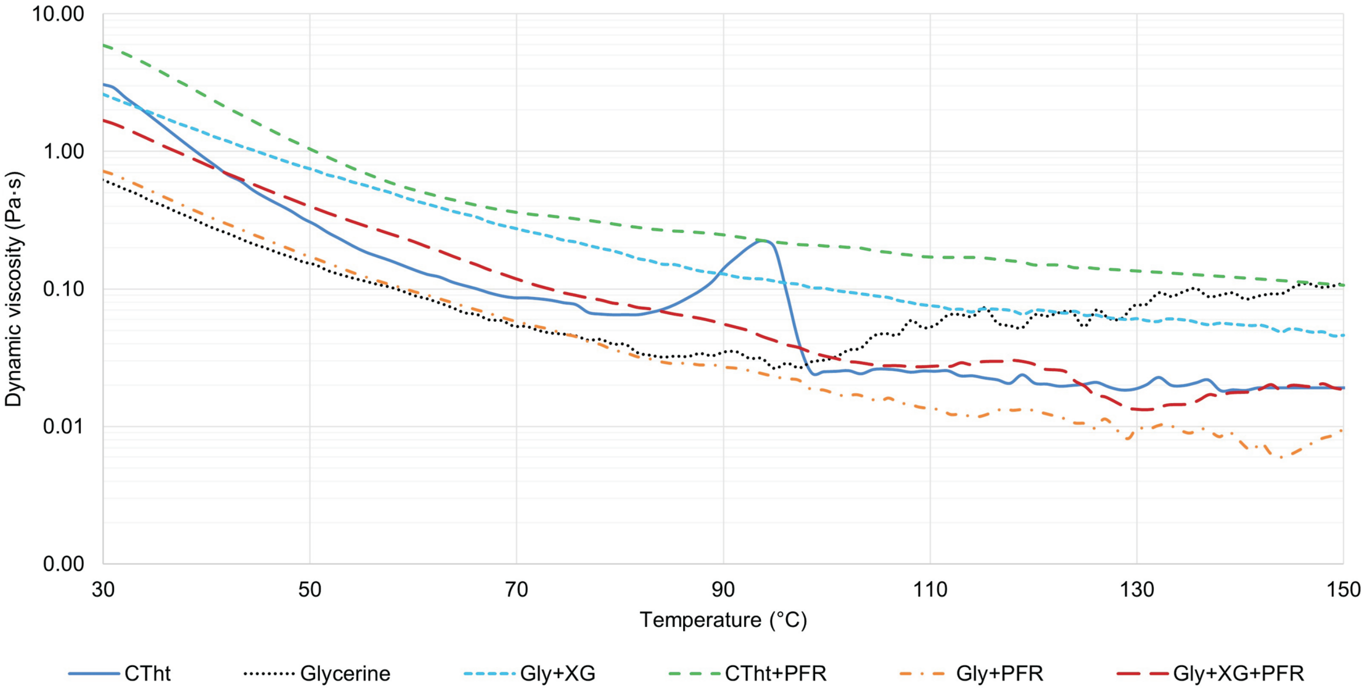

Fig. 10: Change in dynamic viscosity as a function of temperature (thermal stability) of various binders.

structure characterized by polar-polar bonding, making it more resistant to shear deformation. Both the glycerine and resole resin have -OH functional groups (Fig. 2 and Fig. 4, respectively), which makes both polar. This results in weak intermolecular forces (van der Waals) between the molecules that can accommodate a more uniform distribution of shear forces. Compared to the conventional mixture (CTht+PFR) used in taphole clays, which has a higher viscosity but exhibits shear-thinning behaviour, the glycerine-resin mixture would have the same effect on the extrusion pressure if used in a clay. Despite its lower viscosity and Newtonian behaviour, it would result in a lower extrusion pressure during the ramming of the clay.

Dynamic viscosity was also evaluated as a function of temperature, i.e., thermal stability of the molecular structure of the binders/mixtures, where samples were heated from 30 °C to 150 °C at a heating rate of 5 K/min as shown in Fig. 10. The results from Fig. 10 are used only to describe the trends in viscosity changes as a function of temperature, due to differences in viscosity readings between Fig. 9 and Fig. 10 at similar temperatures. These differences arise from the way in which the rheology tests are conducted, as well as the nature of the industrial samples (CTht). During the isothermal rotational test, the samples were soaked at 45 °C for 60 seconds before the measurement began. In contrast, during the temperature sweep, the samples were heated at a rate of 5 K/min, providing less soaking time for the sample to reach equilibrium before the measurement. The industrial samples (CTht) are not sampled in a controlled manner and may contain contaminants such as water droplets. The trends observed from the results in Fig. 10 include how quickly, and if at all, the samples reach a plateau in viscosity when heated up to 150 °C.

The viscosity change in the reference binder (CTht) indicated a decrease in viscosity up to 80 °C, followed by an increase between 80 – 93 °C, and then a plateau. The increase in viscosity shown after 80 °C could be due to rapid volatilization of lower-temperature volatile species in the binder, which influences how the rheometer measures the sample. This is confirmed by the TGA results (Fig. 6), which indicate a mass loss between 70 – 90 °C, possibly causing the increase in viscosity at 80 °C. The viscosity of the glycerine sample decreased up to 85 °C and then increased again up to 150 °C. The viscosity changed by an order of magnitude, from 0.6 Pa·s to 0.02 Pa·s, before increasing again. The increase in viscosity was attributed to the volatilization of lower-temperature volatile species, which caused an irregular reading from the rheometer, similar to the reference sample.

Plasticizing glycerine with xanthan gum resulted in a higher initial viscosity (2.44 Pa·s) compared to pure glycerine. Heating the sample reduced the viscosity up to 114 °C, after which it reached a plateau. The reduction in viscosity from the initial temperature up to 150 °C decreased by more than an order of magnitude. The combination of non-Newtonian and shear-thinning behaviour of this binder, along with its good thermal stability, makes it a favourable alternative binder to pure glycerine.

Mixing coal tar with phenolic resole resin resulted in a higher initial viscosity than the CTht binder, with no indication of the onset of curing of the phenolic resole resin. The viscosity of this mixture decreased up to 65 °C, after which an inflection was reached. This demonstrates the good thermal stability of the binder due to the smaller decrease in viscosity with increasing temperature. Mixing phenolic resin with glycerine resulted in an increase in the initial viscosity because of the higher molecular mass structure. However, compared to the coal tar conventional binder, it exhibited lower thermal stability. Although shear deformation did not permanently alter the molecular structure of the mixture, thermal stimuli made the structure less stable than the coal tar-resin conventional mixture.

Gly+XG+PFR had a lower initial viscosity than the plasticized version (Gly+XG). Mixing the resin with plasticized glycerine resulted in a molecular structure that was more resistant to thermal stimuli, as shown by the higher thermal stability. The decrease in viscosity was an order of magnitude smaller, and a viscosity stability range was close to that of the reference binder.

The desired binder properties of a taphole clay binder are that the mixing of the clay results in the formation of a plastic solid mass (high viscosity) that can be extruded with low pressure (shear thinning) while maintaining the form of the rammable mass inside the tapping channel (thermal stability) up to the curing temperature of the resin. This assists with low-temperature strength as the material is heated to the oxide sintering temperature of the clay. Based on the rheology results, the most suitable binders to replace conventional coal tar are either the (Gly+PFR) or (Gly+XG+PFR) binders.

V. Conclusions

This study examined the behaviour of a conventional coal tar binder used in taphole clays to understand the characteristics that make it an efficient binder. The objective was to investigate glycerine, including mixtures of glycerine and phenolic resole resin, as a potential non-toxic replacement in taphole clays. The glycerine binders were evaluated using the same methods as the reference binder, and the results were compared to coal tar to observe changes and anticipate the effects of directly substituting them into taphole clays. The following conclusions can be drawn from the study:

- The compositional and functional group analysis indicated that the glycerine mixtures are aliphatic compared to the reference binder, which contains aromatic benzene-type compounds. The presence of these benzene-type compounds in the reference binder results in a high toxicity (BE-value) of 1.65, compared to the glycerine alternatives, which have BE-values of zero. The mixtures of glycerine and resole resin contained some of the 16-EPA-PAH species, but at lower concentrations, closer to the permissible exposure limit, which is considered less toxic. The toxicity of the glycerine-based binders is solely dependent on the composition and content of the resole resin used.
- Thermal analysis results indicate that the reference binder has a lower average mass loss (0.28 g/K) that occurs over a wide temperature range (70.8 – 380.4 °C), with a higher carbon yield (10.6 %) compared to the glycerine-based mixtures. The glycerine-based binders have a higher average mass loss (1.57 – 1.79 g/K), over a narrower temperature range (50.0 – 240 °C), with a lower carbon yield (2.5 – 2.8 %). The addition of phenolic resin to the glycerine resulted in higher curing temperatures than pure resole resin, especially when plasticized with xanthan gum. The preferred binder among the glycerine mixtures was the glycerine-resole (Gly+PFR) mixture due to its smallest change in curing temperature between the pure resole and the mixture.
- The glycerine-based binders had lower viscosities compared to the reference binder. Both the reference binder and Gly+PFR binder exhibited Newtonian behaviour, while the plasticized version displayed non-Newtonian, shear-thinning behaviour. The glycerine-based binders showed good thermal stability, and their lower viscosity can provide the benefit of reduced binder consumption and shorter clay ageing compared to the reference binder.
- The preferred alternative binder to conventional coal tar is the glycerine-resole resin mixture due to its lower resin curing temperature compared to the other examined mixtures.

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References

[1] Wang, L., Yin, Y., Qiu, W., Liang, Y., Ruan, G., Zhao, L.: Effects of pitch addition on the properties of environmentally-friendly tap-hole clay, *JCS-Japan*, **125**, [2], 12 – 18, (2017).

[2] Cameron, I.J., Ramjee, S., Garbers-Craig, A.M.: A comparative study between coal tar pitch and lower polycyclic aromatic hydrocarbon (PAH) alternative binders for use in tap-hole clays, *Open Cer.*, **16**, [1], 1 – 12, (2023).

[3] Kitamura, M.: Optimizing Taphole Clay Technology. Tokyo: Shinagawa Technical, **16**, [1], 1 – 5, (2014).
doi: https://doi.org/10.1016/B0-08-043152-6/01662-4.

[4] Allen, D., Ishida, H.: Thermosets: Phenolics, Novolacs, and Benzoxazine. 1st Edition. Cambridge: Pergamon, 2001.

[5] Siva, R., Raffi, M., Srinivasa, R.: Experimental study on environmental friendly tap hole clay for blast furnace, *IOP Conf. Ser.: Mater. Sci. Eng*, **330**, 1 – 13, (2017).
doi: https://doi.org/10.1088/1757-899X/330/1/012056.

[6] Renda, C., Bertholdo, R.: Study of phenolic resin and their tendency for carbon graphitization, *J. Polym. Sci.*, **25**, 241, (2018). doi: https://doi.org/10.1007/s10965-018-1635-y.

[7] Sako, E., Orsolini, H., da Silva, B., Galesi, G.: Graphene-like structured tap hole clay for stable blast-furnace drainage and lower CO_2 emissions. In: Proceeding for the XLII ALAFAR Congress. ALAFAR, Brazil, 2022.

[8] Copetti, G.: Blast Furnace Taphole Clay and Cast House – A Greener Approach. In: Proceedings for the 8th International Conference on Refractories (ICRJ). Jamshedpur, India, 2023.

[9] Nelson, L., Hundermark, R.: The 'tap-hole' – key to furnace performance. In: Proceedings for the Furnace Tapping Conference. SAIMM, Johannesburg, 2014.

[10] Gardziella, A., Pilato, L., Knop, A.: Phenolic Resins: Chemistry, Reactions, Mechanism, 24 – 82, Phenolic Resins, Heidelberg: Springer Berlin, 2000.

[11] Cameron, I.J., Garbers-Craig, A.: Understanding how the Binder System Influences the Properties and Process Performance Indicators of Taphole Clays, In: Refractories Worldforum, Baden-Baden, (2024).

[12] Cameron, I.J.: Investigating premature ageing of blast furnace taphole clay containing a resole resin and liquid pitch binder. Master Dissertation, University of Pretoria, 2021.

[13] Danish, M., Mumtaz, M., Fakhar, M., Rashid, U.: Response surface methodology based optimized purification of the residual glycerol from biodiesel production process, *Chiang Mai J. Sci.*, **44**, [4], 1 – 13, (2016).

[14] Fosu, M., Ofori-Kwakye, K., Kuntworbe, N., Bonsu, M.: Investigation of blends of cashew and xanthan gums as a potential carrier for colonic delivery of ibuprofen, *Int. J. Pharmtech.*, **9**, [7], 369 – 380, (2016).

[15] Bobrowski, A., Grabowska, B.: FTIR method in studies of the resol-type phenolic resin structure in the air atmosphere over certain time intervals, *Metal. and Fou. Eng.,* **41**, [3], 107 – 113, (2015).

[16] Andreikov, E.I., Amosova, I.S., Pervova, M.G.: Determining the content of polycyclic aromatic hydrocarbons in industrial samples of coal tar and pitch, *Coke Chem*, **51**, [8], 321 – 325, (2008).

[17] United States Department of Labor.: Permissible Exposure Limits - OSHA Annotated Table Z-1. https://www.osha.gov/annotated-pels/table-z-1 (accessed 12 January 2023).

[18] National Library of Medicine.: Fluoranthene C16H10. PubChem. https://pubchem.ncbi.nlm.nih.gov/compound/Fluoranthene (accessed 12 January 2023).

[19] New Jersey Department of Health.: Hazardous substance fact sheet - Benz(a)anthracene. https://nj.gov/health/eoh/rtkweb/documents/fs/0193.pdf (accessed 12 January 2023).

[20] New Jersey Department of Health and Senior Services.: Hazardous substance fact sheet - Benzo(b)fluoranthene. https://nj.gov/health/eoh/rtkweb/documents/fs/0208.pdf (accessed 12 January 2023).

[21] New Jersey Department of Health.: Hazardous substance fact sheet - Dibenz(a,h)anthracene. https://nj.gov/health/eoh/rtkweb/documents/fs/0622.pdf (accessed 12 January 2023).

[22] Agilent Technologies.: Safety data sheet - Acenaphthylene Standard (1X1 mL). https://www.agilent.com/cs/library/msds/P-620 – 1_NAEnglish.pdf (accessed 12 January 2023).

[23] Sarika, P., Nancarrow, P., Khansaheb, A., Ibrahim, T.: Bio-based alternatives to phenol and formaldehyde for the production of resins, *Polymers*, **12**, [10], 2 – 24, (2020).
doi: https://doi.org/10.3390/polym12102237.

[24] Siddiqui, H., Mahmood, N., Yuan, Z., Crapulli, F.: Sustainable bio-based phenol-formaldehyde resoles using hydrolytically depolymerized kraft lignin, *Molecules*, **22**, [11], 1 – 19, (2017).
doi: https://doi.org/10.3390/molecules22111850.

[25] Zhang, J., Mei, G., Xie, Z., Zhao, S.: Curing mechanism of phenolic resin binder for oxide-carbon refractories, *ISIJ Int.*, **56**, [1], 44 – 49, (2016).
doi: https://doi.org/10.2355/isijinternational.ISIJINT-2015-260.

[26] De Pretto, A., Lindstad, L.: Health-friendly plugging repair paste. In: Proceedings for the Furnace Tapping Conference. Springer International Publishing, Anaheim, California, USA, 2022.