

Original Research

The Neutralization of Used Sovtol in Electrical Transformers Based on Calcium Oxide and Assessment of the Carbon Footprint in the Gas Phase

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Abstract

The work studied the multicomponent Sovtol-calcium oxide system with the aim of converting toxic chlorine organic molecules into a salt form in the form of calcium chloride. Accordingly, thermodynamic modeling of the process of thermal decomposition of Sovtol ($C_{12}H_5Cl_5-0.9$, $C_6H_3Cl_3-0.1$) and calcium oxide was carried out at a maximum entropy of the system over a wide range of temperatures. The values of change in entropy, enthalpy, and the viscosity parameters of the system (dynamic viscosity, Prandtl number) were calculated. The concentration distributions of C, O, H, Cl, and Ca-containing components and charged particles in the gas phase were established, and, on their basis, the contents of carbon and chlorine fragments at 2893 K were calculated. Reduction of the anthropogenic chlorine load from the organic molecule in the gas phase was achieved by preparing a water-suspension fuel emulsion (comprising fuel oil and spent Sovtol) with calcium oxide as solid additives and combusting the mixture in medium- and small-capacity boiler units. Based on the chemical matrix of the initial Sovtol-calcium oxide system, an assessment of the carbon load in the gas phase was carried out.

Keywords: sovtol, calcium oxide, concentration distribution, gas phase, carbon footprint

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Introduction

Transformers are extensively utilized in various industries to convert electric current and voltage. To prevent short circuits and cool metal surfaces, they rely on different types of oils, including industrial polychlorinated biphenyls (PCBs), marketed under various commercial names across the globe [1-3]: Arochlor (USA), Pyralene and Fenochlor (France), Askarel (UK), Clofen (Germany), Canechlor (Japan), Delor (Czechoslovakia), and Sovol and Sovtol-10 (Russia).

The Kyrgyz Republic did not produce polychlorinated biphenyls (PCBs) or PCB-containing equipment. Instead, these substances were primarily imported as components of electrical equipment, transformer oils, paints, varnishes, and various lubricants [2]. Notably, older electrical equipment – such as capacitors (brands: KS, ESV, PS from Russia; KS and KSTA AEG Hydrowerk from Germany) and electric transformers (types: TIPU, TNP, TNZ from Russia; ZWAR from Poland; BICC and HUNTS from England; ZEZ, CTAE, and CU from the Czech Republic) – commonly used mixtures of pentachlorobiphenyl and trichlorobenzene in a 9:1 weight ratio (Sovtol-10) or their equivalents [1]. Sovtol-10 replaced traditional transformer oil as it is a completely non-flammable dielectric material, ensuring fire safety at facilities [1]. However, PCB-containing liquids are classified as persistent organic pollutants and remain a significant problem for ecosystems due to their high resistance and bioaccumulative properties. These substances are resistant to environmental and biological degradation, decompose over decades, and contribute to accumulation processes in animal organisms while migrating through water, air, and microorganisms [4].

A profitable alternative to Sovtol-based transformers is dry-type transformers with cast insulation and oil transformers that use mineral oil [5]. Dry transformers with natural air cooling, featuring windings made from aluminum or copper wire, are explosion-proof, fire-resistant, environmentally friendly, and easy to maintain. These transformers use insulation made from synthetic aramid materials, such as “Nomex” by DuPont (USA) and “Trihal” by Schneider Electric (France) [6, 7]. Additionally, transformers filled with environmentally neutral, non-flammable synthetic and silicone-based liquids have been developed, including “Formel NF” and “Midel 7131” (Great Britain) [8, 9]. As substitutes for PCBs in transformers and capacitors, the following materials are used: mineral and silicone oils, high-molecular-weight paraffins, alkylated biphenyls, and triphenyls, as well as esters of phosphoric, phthalic, and other carboxylic acids and complex esters of polyhydric alcohols [10-13].

Among industrial wastes, the disposal of PCB-based technological fluids remains a significant challenge [14]. This necessitates rigorous methods for physicochemical diagnostics and analysis of concepts related to the best available technologies and green chemistry [15].

In recent years, non-volatile metal oxides capable of forming thermally stable low-molecular-weight chlorides in a gas-liquid medium have been used to address this issue. In this regard, alkaline earth metal oxides and their double carbonates, such as dolomite, are particularly effective and readily available reagents for the disposal of PCB-based technical mixtures through blast furnace smelting [16-18] and thermal desorption of chlorine from PCB molecules [19]. In this context, the study in [20] examined the synergistic thermal desorption process with the addition of calcium hydroxide for the decontamination of soil collected from storage sites for PCB-contaminated capacitors and transformers. This process was carried out at temperatures ranging from 300 to 600°C using both natural soil (1) and model soil with 1% added Ca(OH)_2 (2). Dechlorination was found to be significantly more effective in (2) compared to (1). Calcium hydroxide enhanced the removal, dechlorination, and detoxification of PCBs. In [21], calcium oxide and persulfate were used as reagents for co-grinding in a mechanochemical process, showing the degradation of hexachlorobenzene in contaminated soil. Photocatalytic degradation of PCBs combined with soil washing, iron-based reductive dechlorination, and persulfate oxidation proved highly effective [22]. Furthermore, PCB degradation using metallic calcium nanoparticles in CaO at 250°C under dry solid-state conditions was noted. This process was applied to PCB-contaminated soil, completely eliminating toxic polychlorinated compounds [23]. The study in [24] investigated the degradation of 4-bromochlorobenzene (4-BCB), which contains both chlorine and bromine, via mechanochemical destruction using CaO powder. The CaO powder was converted into CaCl_2 , CaBr_2 , Ca(OH)_2 , and CaCO_3 . Similarly, in [25], lindane degradation in soil was primarily attributed to the mechanical activation of CaO, leading to the generation of free electrons and alkalinity from the resulting Ca(OH)_2 . In [26], Ca and CaO were used to adsorb acidic gasses (HCl , Cl_2 , and SO_x) in waste incineration plants. It was emphasized that CaO significantly suppressed the chlorination of the carbon matrix and the formation of unsaturated hydrocarbons or aromatic carbon. Moreover, CaO facilitated the dechlorination of Cu-based catalysts and the stabilization of chlorine by converting CuCl_2 into CuO and forming CaCl_2 .

Thus, studies utilizing calcium oxide for PCB destruction have primarily focused on soil and included processes such as hydrodechlorination, simple reduction, reductive binding, and hydroxylation [23]; breaking the benzene ring in PCBs to form small molecular halogenated hydrocarbons, followed by their mineralization into CO_2 , H_2O , and graphite [24]; dechlorination via elimination, alkaline hydrolysis, hydrogenolysis, and subsequent carbonation [25]; substitution of the Cl bond in the benzene ring with -OH, inhibiting the polycondensation of chlorobenzene and chlorophenol, indicating the effective dechlorinating effect of CaO in suppressing the synthesis of toxic substances [26]; and detoxification of

PCB-based technical mixtures through blast furnace smelting [16-19].

The hydrothermal detoxification processes for chlorinated organic compounds are generally inefficient due to the extremely low solubility of PCBs in water at standard temperatures. However, under subcritical conditions, the significantly increased solubility of organic substances in water enhances their chemical reactivity and reaction rates with increasing temperature, making hydrolytic decomposition of polychlorinated biphenyls feasible [27].

Considering these circumstances, this study investigates the Sovtol-calcium oxide system to detoxify toxic chlorine in organic molecules by burning a water-suspension fuel emulsion prepared from a mixture of fuel oil, Sovtol, and water, with calcium oxide as solid additives. The carbon footprint was calculated based on the concentration distribution of carbon-containing active particles, components, and condensed phases in the gas phase.

Materials and Methods

Processes for the neutralization and disposal of Sovtol under practical conditions have typically been based on instrumental studies [28-31], but these methods are costly and pose safety risks. Considering these circumstances, we employed thermodynamic modeling using the "Terra" software package [32, 33] to predict and gather essential information about the composition of emissions, as well as the formation, transformation, and behavior of various substances during Sovtol destruction in a calcium oxide medium over a wide temperature range. Determining the coordinates of the conditional entropy maximum in the program was performed using the Lagrange multipliers method [32].

The equilibrium composition of the mixture at a given pressure (P) and temperature (T) was established by solving dissociation reaction equations for molecular components into atomic ones. These calculations took into account thermodynamic potentials (U, S, I) as a function of temperature, material balance equations, and the conditions for the formation of condensed phases. The unknowns were the logarithms of the molar quantities of individual substances and the mass fractions of chemical elements in the mixture (M_s), which consisted of Sovtol and calcium oxide. The task was reduced to determining the M_s fragments through iterative methods [32, 33].

Calcium oxide was chosen as the preferred reagent for Sovtol neutralization processes due to its synergistic effects on the molecular components of Sovtol. These effects are attributed to the processes described in [23, 34], which include the formation of low-molecular-weight halogenated hydrocarbons and their mineralization into chloride salts, CO₂, H₂O, and condensed carbon. This transformation of chlorinated organic compounds into a salt form proved to be the most efficient

approach. Accordingly, the calculations considered the system Sovtol (C₁₂H₅Cl₅ /0.9/ + C₆H₃Cl₃ /0.1/) – calcium oxide (CaO /1.0/) with the following elemental composition (mol/kg): C – 18.196, H – 7.719, Cl – 7.719, Ca – 8.916, O – 8.916. The temperature range (293-3000 K) encompassed the decomposition temperatures of both the initial and resulting substances: CaO (2843 K), Ca(OH)₂ (853 K), CaCO₃ (1098 K), CaCl₂ (1045 K), and Sovtol (598-639 K) [35].

The study calculated the equilibrium compositions of components, atomic particles, and condensed phases. Based on the concentration distribution of carbon-containing particles in the gas phase, the additive carbon footprint was determined for Sovtol decomposition, considering the number of carbon atoms and moles in the organic molecule [36]. A conceptual technological scheme was developed for preparing a water-suspension fuel emulsion (fuel oil + spent Sovtol) using calcium oxide as solid additives [37], achieving the neutralization of spent Sovtol in the gas phase.

Results and Discussion

Neutralizing chlorine-containing substances in Sovtol within the gas phase was achieved using calcium oxide, a product of calcium carbonate decomposition at high temperatures (1273 K). The total content of chlorine-containing substances in the gas phase included (T = 793-3000 K, P = 0.1 MPa, Table 1): Cl, Cl₂, ClO, HCl, HOCl, CCl, CCl₂, C₂Cl, C₂Cl₂, ClCO, Cl₂CO, CHCl, CH₂Cl, CH₃Cl, CHCl₂, CH₂Cl₂, C₂HCl, C₂H₃Cl, C₂H₂Cl₂, HClCO, CaCl, CaCl₂, CaOHCl, Cl⁻, CaCl⁺. The cumulative presence of these substances was determined by passing gasses through a filter connected to a condenser, with the collected condensate analyzed for content [37].

Below are comparative results of the physicochemical modeling of Sovtol thermodestruction in the following environments:

- (I) Metal oxides (Ba, Al, Ca, Mg) (Fig. 1a))
- (II) Metal oxides (Ba, Al, Ca, Mg) – water – oxygen (Fig. 1b)), as reported in previous studies [14, 27, 34]
- (III) The Sovtol-calcium oxide system (Fig. 2), investigated in the present study.

The data highlight the temperature ranges for forming all chlorine-containing substances and active species in the gas phase. It was emphasized that the optimal temperature for chlorine binding from Sovtol molecules and its conversion into salt form lies within 1600–1700 K. In this range, the concentration of calcium chloride, including condensed calcium chloride, is significantly higher in system (III) (3.75 mol/kg) compared to (I) (2.25 mol/kg) and (II) (1.2 mol/kg at 1500 K).

System (III) demonstrated more complete hydrodechlorination, reductive binding, and hydroxylation. This is attributed to the breakdown of the benzene ring in PCBs, forming small molecular

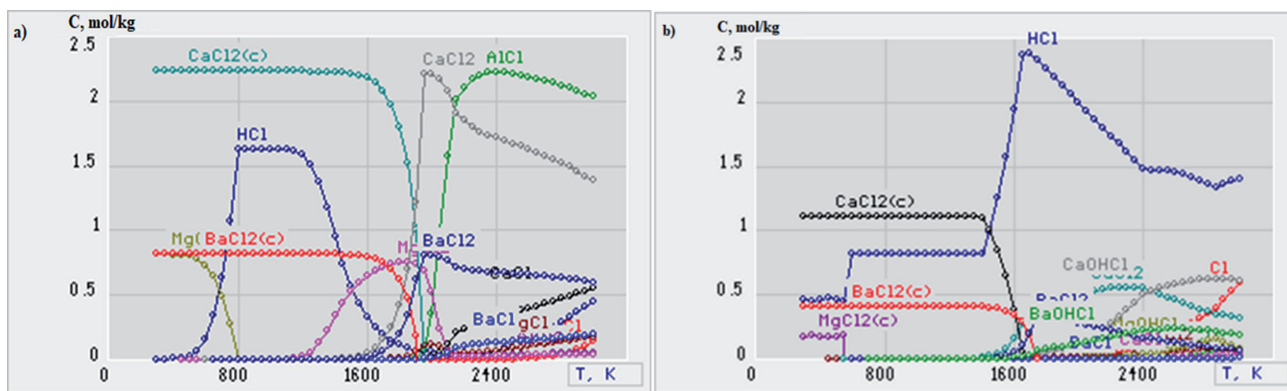


Fig. 1. a) Thermodestruction of Sovtol in the environment of metal oxides (Ca, Mg, Ba, Al); b) conversion of Sovtol in the environment of metal oxides (Ca, Mg, Ba, Al) with water and oxygen, and the distribution of chlorine-containing components and particles in the gas phase, depending on temperature [14, 27, 34].

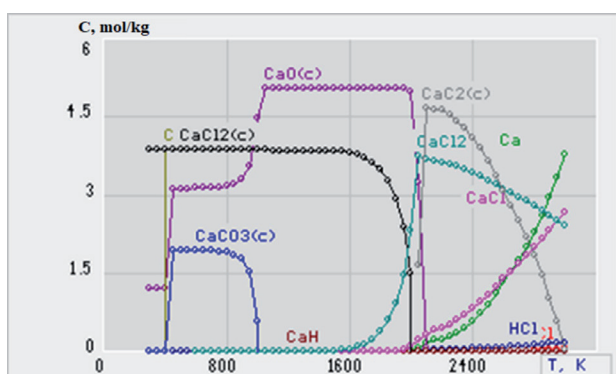


Fig. 2. Thermodestruction of Sovtol in the environment of calcium oxide and the distribution of chlorine-containing components and particles in the gas phase, depending on temperature.

halogenated hydrocarbons and their mineralization into CO₂, H₂O, and condensed carbon (Table 1). Substitution of single Cl bonds with -OH in the benzene ring inhibited the polycondensation of chlorobenzene, indicating the effective dechlorinating effect of CaO in neutralizing Sovtol. This effect is particularly pronounced in the 1173-1273 K range, where calcium carbonate decomposes into calcium oxide (CaO). In this

environment, significant amounts of condensed phases form, including CaO(c), CaCl₂(c), as well as chlorides such as CaCl₂, CaCl, HCl, calcium carbide (CaC₂), and calcium hydride (CaH) (Fig. 2).

The direction and progression of the decomposition processes of the initial substances, the calculation of individual thermochemical parameters (Lt, Cp) of the system based on the work [35], as well as the formation of calcium- and chlorine-containing molecules and particles, are confirmed by the negative values of the enthalpy in the Sovtol–calcium oxide system (Fig. 3a)). Additionally, this is supported by the entropy extrema of individual components (Fig. 3b)) and the variation of the Prandtl number within 0.4 for substances present in the gas phase (Fig. 3c)).

In the modeling calculations, the logarithms of the number of moles of individual substances and the mass fraction of chemical elements in the mixture (Ms – comprising Sovtol and calcium oxide – were considered unknowns. As previously noted, the task was reduced to determining the (Ms) fragments using the iterative method [32, 33], and the obtained results are presented in Table 1.

From Table 1, it can be seen that toxic Sovtol decomposes with the release of active chlorine, and its

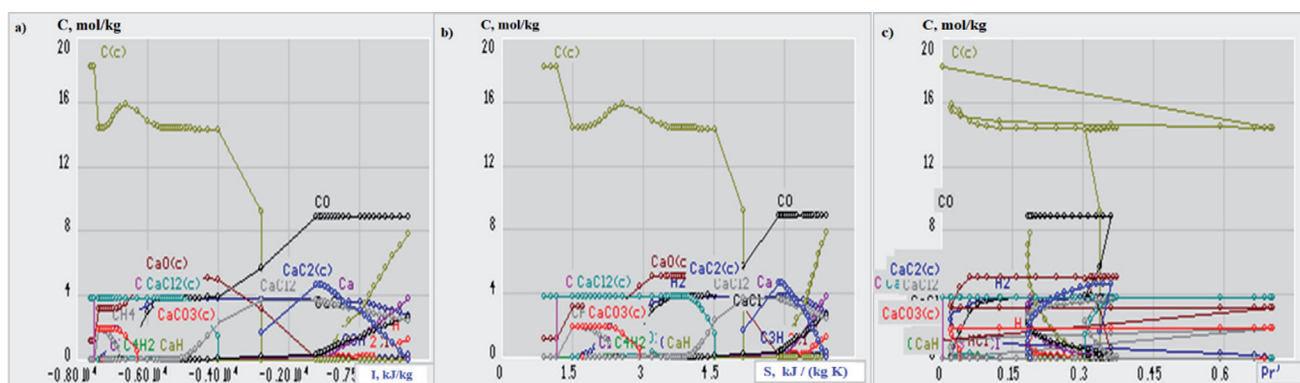


Fig. 3. Variation in a) enthalpy, b) entropy, and c) Prandtl number of the Sovtol–calcium oxide system at T = 2893 K, P = 0.1 MPa.

Table 1. The concentration distribution of carbon and chlorine-containing particles, molecules, and condensed phase (mol.kg⁻¹) in the gas phase depending on the decomposition temperature of the system components. P = 0.1 MPa.

Molecules and particles, mol kg ⁻¹	T, K					
	793	1293	1793	2293	2793	2993
C _(s)	15.1	14.35	14.34	0.40	5.12	7.80
C	-	-	0.16×10 ⁻¹¹	0.12×10 ⁻⁶	0.12×10 ⁻³	0.001
C ₂	-	-	-	0.21×10 ⁻⁷	0.55×10 ⁻⁴	0.64×10 ⁻³
C ₃	-	-	-	0.25×10 ⁻⁶	0.58×10 ⁻³	0.006
C ₄	-	-	-	0.63×10 ⁻¹⁰	0.10×10 ⁻⁵	0.21×10 ⁻⁴
C ₅	-	-	-	0.28×10 ⁻⁹	0.54×10 ⁻⁵	0.11×10 ⁻³
CO	0.004	3.81	3.85	8.91	8.91	8.91
CO ₂	0.81×10 ⁻³	0.010	0.14×10 ⁻³	0.35×10 ⁻⁴	0.72×10 ⁻⁵	0.42×10 ⁻⁵
C ₂ O	-	-	0.46×10 ⁻⁹	0.41×10 ⁻⁶	0.18×10 ⁻⁴	0.61×10 ⁻⁴
C ₃ O ₂	-	0.6×10 ⁻¹¹	0.17×10 ⁻⁹	0.29×10 ⁻⁸	0.88×10 ⁻⁸	0.11×10 ⁻⁷
CH	-	-	0.14×10 ⁻¹⁰	0.12×10 ⁻⁶	0.32×10 ⁻⁴	0.17×10 ⁻³
CH ₂	-	-	0.80×10 ⁻⁸	0.19×10 ⁻⁵	0.59×10 ⁻⁴	0.14×10 ⁻³
CH ₃	0.5×10 ⁻¹⁰	0.45×10 ⁻⁶	0.14×10 ⁻⁴	0.69×10 ⁻⁴	0.18×10 ⁻³	0.19×10 ⁻³
CH ₄	1.17	0.01	0.001	0.18×10 ⁻³	0.55×10 ⁻⁴	0.28×10 ⁻⁴
C ₂ H	-	-	0.12×10 ⁻⁷	0.42×10 ⁻⁴	0.006	0.02
C ₂ H ₂	0.1×10 ⁻¹¹	-	0.67×10 ⁻³	0.016	0.113	0.178
C ₂ H ₃	-	0.39×10 ⁻⁹	0.21×10 ⁻⁶	0.50×10 ⁻⁵	0.36×10 ⁻⁴	0.52×10 ⁻⁴
C ₂ H ₄	0.13×10 ⁻⁶	0.31×10 ⁻⁵	0.75×10 ⁻⁵	0.57×10 ⁻⁵	0.51×10 ⁻⁵	0.36×10 ⁻⁵
C ₂ H ₂ O	-	0.21×10 ⁻⁵	-	-	-	-
C ₂ H ₅	-	0.10×10 ⁻⁹	0.90×10 ⁻⁹	0.94×10 ⁻⁹	0.11×10 ⁻⁸	0.83×10 ⁻⁹
C ₂ H ₆	0.17×10 ⁻⁴	0.85×10 ⁻⁷	0.48×10 ⁻⁸	0.21×10 ⁻⁹	0.40×10 ⁻¹⁰	0.1×10 ⁻¹⁰
C ₃ H	-	-	0.91×10 ⁻⁷	0.38×10 ⁻³	0.06	0.28
C ₃ H ₄	-	-	0.26×10 ⁻¹⁰	0.55×10 ⁻⁹	0.44×10 ⁻⁸	0.57×10 ⁻⁸
C ₃ H ₈	0.12×10 ⁻⁸	0.1×10 ⁻¹¹	-	-	-	-
C ₄ H	-	-	-	0.54×10 ⁻⁷	0.51×10 ⁻⁴	0.40×10 ⁻³
C ₄ H ₂	-	0.3×10 ⁻¹⁰	0.10×10 ⁻⁵	0.33×10 ⁻³	0.001	0.02
C ₄ H ₄	-	-	-	0.25×10 ⁻⁴	0.53×10 ⁻¹⁰	0.9×10 ⁻¹⁰
CHO	-	0.11×10 ⁻⁷	0.54×10 ⁻⁶	0.77×10 ⁻⁵	0.27×10 ⁻⁴	0.37×10 ⁻⁴
CHO ₂	-	0.9×10 ⁻¹¹	0.12×10 ⁻¹⁰	0.28×10 ⁻¹⁰	0.26×10 ⁻¹⁰	0.2×10 ⁻¹⁰
CH ₂ O	0.15×10 ⁻⁸	0.91×10 ⁻⁶	0.77×10 ⁻⁶	0.79×10 ⁻⁶	0.59×10 ⁻⁶	0.45×10 ⁻⁶
CH ₂ O ₂	0.26×10 ⁻⁹	0.60×10 ⁻⁸	0.10×10 ⁻⁹	0.15×10 ⁻¹⁰	0.27×10 ⁻¹¹	0.13×10 ⁻⁹
CH ₃ O	-	-	-	-	0.13×10 ⁻¹¹	0.1×10 ⁻¹¹
CCl	-	-	0.11×10 ⁻¹¹	0.11×10 ⁻⁷	0.58×10 ⁻⁵	0.41×10 ⁻⁴
CCl ₂	-	-	-	0.26×10 ⁻¹¹	0.13×10 ⁻⁸	0.10×10 ⁻⁷
C ₂ Cl	-	-	-	0.28×10 ⁻⁸	0.23×10 ⁻⁵	0.19×10 ⁻⁴
C ₂ Cl ₂	-	-	-	0.24×10 ⁻¹⁰	0.11×10 ⁻⁷	0.74×10 ⁻⁷
ClCO	-	-	0.81×10 ⁻¹⁰	0.60×10 ⁻⁸	0.11×10 ⁻⁶	0.28×10 ⁻⁶
Cl ₂ CO	-	-	-	-	0.18×10 ⁻¹¹	0.4×10 ⁻¹¹
CHCl	-	-	0.35×10 ⁻¹¹	0.32×10 ⁻⁸	0.41×10 ⁻⁶	0.17×10 ⁻⁵
CH ₂ Cl	-	0.2×10 ⁻¹¹	0.68×10 ⁻⁹	0.25×10 ⁻⁷	0.46×10 ⁻⁶	0.99×10 ⁻⁶
CH ₃ Cl	0.2×10 ⁻¹⁰	0.85×10 ⁻⁸	0.13×10 ⁻⁷	0.17×10 ⁻⁷	0.42×10 ⁻⁷	0.43×10 ⁻⁷
CHCl ₂	-	-	-	0.45×10 ⁻¹¹	0.52×10 ⁻⁹	0.21×10 ⁻⁸
CH ₂ Cl ₂	-	-	-	-	0.17×10 ⁻¹⁰	0.3×10 ⁻¹⁰
C ₂ HCl	-	-	0.52×10 ⁻⁸	0.12×10 ⁻⁵	0.69×10 ⁻⁴	0.22×10 ⁻³



C ₂ H ₃ Cl	-	0.1×10 ⁻¹⁰	0.31×10 ⁻⁹	0.19×10 ⁻⁸	0.12×10 ⁻⁷	0.18×10 ⁻⁷
C ₂ H ₂ Cl ₂	-	-	-	-	0.61×10 ⁻¹¹	0.1×10 ⁻¹⁰
HClCO	-	0.2×10 ⁻¹⁰	0.10×10 ⁻⁹	0.58×10 ⁻⁹	0.24×10 ⁻⁸	0.34×10 ⁻⁸
C ⁻	-	-	-	-	0.61×10 ⁻⁹	0.10×10 ⁻⁷
C ₂ ⁻	-	-	-	0.10×10 ⁻⁸	0.32×10 ⁻⁵	0.38×10 ⁻⁴
CaCO ₃ (s)	1.89	-	-	-	-	-
CaC ₂ (s)	-	-	-	4.41	1.83	0.037

interaction with calcium oxide in the gas phase leads to the formation of thermally stable calcium chlorides, which, after cooling, are directed into slag phases. Numerous carbon-containing components, particles, and condensed phases are observed in the gas phase at T = 2893 K: C(c), C, C₂, C₃, C₄, C₅, CO, CO₂, C₂O, C₃O₂, CH, CH₂, CH₃, CH₄, C₂H, C₂H₂, C₂H₃, C₂H₄, C₂H₅, C₂H₆, C₃H, C₃H₄, C₄H, C₄H₂, C₄H₄, CHO, CHO₂, CH₂O, CH₂O₂, CH₃O, CCl, CCl₂, C₂Cl, C₂Cl₂, ClCO, Cl₂CO, CHCl, CH₂Cl, CH₃Cl, CHCl₂, CH₂Cl₂, C₂HCl, C₂H₃Cl, C₂H₂Cl₂, HClCO, CaC₂(c), C⁻, C₂⁻ (Table 2).

Based on the concentration distribution of particles in the gas phase (Table 1), the carbon footprint (Table 2) [38-40], as well as the chlorine load (Table 3), was calculated for the system: C₁₂H₅Cl₅ (0.9) – C₆H₃Cl₃ (0.1) – CaO (1). It should be noted that the specific direct emissions of greenhouse gasses (e₁) are determined using the following formula, where carbon dioxide, methane, and nitrous oxide in the gas phase result from the oxidation of carbon-containing substances [38]:

$$e_1 = \frac{E_1}{V_{\text{output}}} = \frac{\sum_{i=1}^N (B_i K_i^{\text{CO}_2} + 25 B_i K_i^{\text{CH}_4} + 298 B_i K_i^{\text{N}_2\text{O}})}{V_{\text{output}} \left(\frac{t\text{CO}_2 \text{ eq}}{t} \right)}$$

Where: Global warming potentials: CO₂ – 1,0; CH₄ – 25; N₂O-298; K_i^{CO₂}, K_i^{CH₄}, K_i^{N₂O}- emission factors for various source categories; B_i – actual annual fuel consumption, in tons of standard fuel; E₁ – annual volume of direct emissions, in t CO₂ equivalent; V_{output} – annual production volume, in tons.

A precise calculation of E₁, i.e., the volume of direct emissions in t CO₂ equivalent, requires determining the additive value of the carbon load across all fragments formed during the decomposition of Sovtol. This calculation takes into account the number of carbon atoms and moles in the molecule of the organic component (Table 2). It is noted that the initial weight content of carbon in the sovtol-calcium oxide system is 18.966 mol/kg, i.e., 227.592 g C. During the decomposition of sovtol in a calcium oxide medium at T = 2893 K, in accordance with the data in Table 2, the total carbon content is equal to 218.092 g C, or 0.79 t CO₂ eq, which is useful for assessing the carbon footprint per unit of product. From the data obtained, it is clear

Table 2. Calculation of carbon load in the gas phase during thermal decomposition of the system: C₁₂H₅Cl₅ (0.9)-C₆H₃Cl₃ (0.1)-CaO (1). T = 2893 K.

Components and particles in the gas phase	Content, mol kg ⁻¹	Carbon, in grams
C _(c)	6.41	76.76
C	0.37×10 ⁻³	4.5×10 ⁻³
C ₂	0.19×10 ⁻³	4.7×10 ⁻³
C ₃	2.04×10 ⁻³	7.3×10 ⁻²
C ₄	0.49×10 ⁻⁵	2.38×10 ⁻⁴
C ₅	0.26×10 ⁻⁴	1.58×10 ⁻³
CO	8.91	106.9
CO ₂	0.55×10 ⁻⁵	6.6×10 ⁻⁵
C ₂ O	0.34×10 ⁻⁴	8.4×10 ⁻⁴
C ₃ O ₂	0.10×10 ⁻⁷	4.9×10 ⁻⁷
CH	0.76×10 ⁻⁴	9.24×10 ⁻⁴
CH ₂	0.96×10 ⁻⁴	1.15×10 ⁻³
CH ₄	0.41×10 ⁻⁴	4.92×10 ⁻⁴
C ₂ H	0.01	0.31
C ₂ H ₂	0.14	3.5
C ₂ H ₃	0.45×10 ⁻⁴	1.08×10 ⁻³
C ₂ H ₄	0.45×10 ⁻⁵	1.1×10 ⁻⁴
C ₂ H ₅	0.10×10 ⁻⁸	2.5×10 ⁻⁸
C ₂ H ₆	0.25×10 ⁻¹⁰	6.24×10 ⁻¹⁰
C ₃ H	0.13	4.89
C ₃ H ₄	0.51×10 ⁻⁸	1.85×10 ⁻⁸
C ₄ H	0.15×10 ⁻³	7.2×10 ⁻³
C ₄ H ₂	0.01	0.91
C ₄ H ₄	0.75×10 ⁻¹⁰	3.65×10 ⁻⁹
CHO	0.32×10 ⁻⁴	3.96×10 ⁻⁴
CHO ₂	0.25×10 ⁻¹⁰	0.3×10 ⁻⁹
CH ₂ O	0.53×10 ⁻⁶	0.64×10 ⁻⁵
CH ₂ O ₂	0.19×10 ⁻¹¹	2.34×10 ⁻¹¹
CH ₃ O	0.13×10 ⁻¹¹	1.63×10 ⁻¹¹

CCl	0.16×10^{-4}	1.96×10^{-3}
C ₂ Cl	0.70×10^{-5}	1.7×10^{-4}
C ₂ Cl ₂	0.29×10^{-7}	0.72×10^{-7}
CICO	0.18×10^{-6}	0.2×10^{-5}
Cl ₂ CO	0.30×10^{-11}	0.37×10^{-10}
CHCl	0.88×10^{-6}	1.06×10^{-5}
CH ₂ Cl	0.70×10^{-6}	0.85×10^{-5}
CH ₃ Cl	0.44×10^{-7}	0.54×10^{-6}
CHCl ₂	0.11×10^{-8}	1.32×10^{-8}
CH ₂ Cl ₂	0.26×10^{-3}	0.32×10^{-9}
C ₂ HCl	0.12×10^{-3}	3.12×10^{-3}
C ₂ H ₃ Cl	0.16×10^{-7}	0.38×10^{-6}
C ₂ H ₂ Cl ₂	0.11×10^{-10}	0.26×10^{-9}
HCICO	0.29×10^{-8}	0.36×10^{-7}
CaCl _{2(c)}	1.02	24.72
C ⁻	0.26×10^{-8}	3.14×10^{-8}
C ₂ ⁻	0.11×10^{-4}	1.39×10^{-4}

that 4.2 g of carbon is lost due to the exergy of the flow, i.e., due to the dissipation of particles inside and outside the system when it interacts with the environment. It should be noted here that during the decomposition of carbon-containing Sovtol in a calcium oxide environment (T = 2893 K), the carbon footprint in the gas phase is mainly due to (%): CO – 49.02; C_(e) – 35.2; CaC_{2(c)} – 11.33; S₃N – 2.24; C₂H₂ – 1.6; C₄H₂ – 0.42; C₂H – 0.14 (Table 2), the remaining particles are contained within 0.047%.

Table 3 presents the calculation of the chlorine load in the gas phase during the decomposition of the system: C₁₂H₅Cl₅(0.9)-C₆H₃Cl₃(0.1)-CaO(1), T=2893 K, and epy limiting stages of the transfer of toxic chlorine from the Sovtol molecule to hydrogen chloride (HCl – 5.14 g), calcium chloride (CaCl – 82.4 g, CaCl₂ – 185.3 g), and atomic chlorine (Cl – 1.03 g) were identified; and the remaining part of chlorine-containing particles is only 0.053 g; the total mass of chlorine-containing fragments after the decomposition of Sovtol is 273.92 g, and in the original Sovtol – 274.02 g Cl. Thus, the toxic Sovtol chlorine is almost completely converted into a salt form of calcium chloride and hydrogen chloride ($273.92/274.02 = 99.96\%$).

In order to neutralize Sovtol in practical conditions, a basic technological scheme has been developed for the preparation and combustion of a water-suspension fuel emulsion [37], where used Sovtol is taken from an old electric transformer in compliance with safety regulations [2], before the oil is mixed with mazut (→). The liquid mixture, after passing through the coarse filters (I and II), is fed into the rotary pulsation

Table 3. Calculation of the chlorine load in the gas phase during thermal decomposition of the system: C₁₂H₅Cl₅(0.9)-C₆H₃Cl₃(0.1)-CaO(1). T = 2893 K.

Components and particles in the gas phase	Content, mol kg ⁻¹	Chlorine, in grams
Cl	0.02	1.03
Cl ₂	0.64×10^{-6}	4.5×10^{-5}
CIO	0.37×10^{-10}	1.31×10^{-9}
HCl	0.14	5.14
HOCl	0.12×10^{-10}	4.33×10^{-10}
CCl	0.16×10^{-4}	5.68×10^{-4}
CCl ₂	0.39×10^{-8}	0.85×10^{-8}
C ₂ Cl	0.71×10^{-5}	2.5×10^{-4}
C ₂ Cl ₂	0.30×10^{-7}	2.13×10^{-6}
CICO	0.11×10^{-6}	6.74×10^{-6}
Cl ₂ CO	0.31×10^{-11}	0.43×10^{-11}
CHCl	0.88×10^{-6}	3.12×10^{-5}
CH ₂ Cl	0.71×10^{-6}	2.5×10^{-5}
CH ₃ Cl	0.45×10^{-7}	1.16×10^{-6}
CHCl ₂	0.11×10^{-8}	7.81×10^{-8}
CH ₂ Cl ₂	0.27×10^{-10}	1.9×10^{-9}
C ₂ HCl	0.12×10^{-3}	4.61×10^{-3}
C ₂ H ₃ Cl	0.16×10^{-7}	5.68×10^{-7}
C ₂ H ₂ Cl ₂	0.11×10^{-10}	7.81×10^{-10}
HCICO	0.29×10^{-8}	1.06×10^{-7}
CaCl	2.32	82.4
CaCl ₂	2.61	185.3
CaOHCl	0.54×10^{-4}	1.92×10^{-3}
Cl ⁻	1.04×10^{-3}	3.7×10^{-2}
CaCl ⁺	0.28×10^{-3}	9.94×10^{-3}

apparatus RPA (V and VI). Shredded calcium carbonate from the mill (32) through sieves (33) is sent to the storage hopper (34) and then to the vibrating feeder (36). In the ultrasonic generator, the solid phase is mixed with oil-contaminated water from the water tank (VII) and then ejects (41) into the RPA, where a water-suspension fuel emulsion is formed (Fig. 4).

The resulting inverse emulsion (85% mazut-oil and 15% water suspension) is supplied to the nozzles, and in the high-temperature combustion zone, the fuel mixture, calcium carbonate, is converted into calcium oxide. In the gas phase, the formation of hydrogen chloride (HCl) and calcium chloride (CaCl, CaCl₂) was noted, and thus the neutralization of toxic Sovtol was achieved.

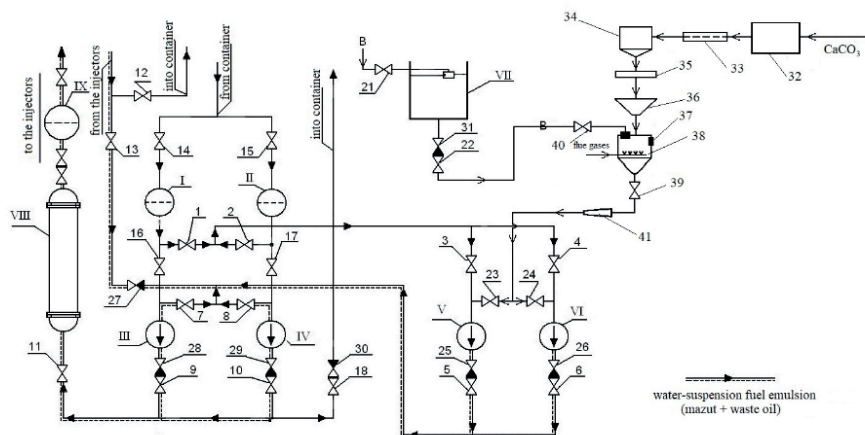


Fig. 4. Schematic flow diagram of the system for preparing and burning a water-suspension fuel emulsion [37]: I, II – coarse filters; III, IV – gear pumps; V, VI – rotary pulsation devices (RPA); VII – water tank; VIII – mazut and waste oil heater; IX – fine filter; 1–24 – gate valves; 25–31 – check valves; 32 – mill; 34 – storage hopper; 33, 35 – sieves; 36 – vibration dispenser; 37 – ultrasonic generator; 38 – mixer with liquid level regulator; 39, 40 – valves; 41 – ejector.

Conclusions

The multicomponent Sovtol-calcium oxide system was studied under a wide range of temperatures ($T = 298\text{--}3000\text{ K}$, $P = 0.1\text{ MPa}$). Equilibrium parameters were calculated, and concentration distributions of C, H, O, Cl, and Ca-containing components and active particles in the gas phase were determined. Based on the total concentration distribution of carbon-containing components and active particles, the weight content of carbon in the gas phase was calculated. Taking into account the chemical matrix of the Sovtol-calcium oxide system and the weight content of carbon, the value of the carbon load ($0.79\text{ t CO}_2\text{ eq}$) in the gas phase was calculated, which is useful in estimating the carbon capacity per unit of production. In order to neutralize Sovtol in practical conditions, a basic technological scheme for the preparation and combustion of water-suspension fuel emulsion in medium- and low-power boilers has been developed. At the same time, the formation of hydrogen chloride and calcium chloride was noted, and the neutralization of toxic Sovtol in the gas phase was achieved.

Conflict of Interest

The authors declare no conflict of interest.

References

- KUKHARCHIK T.I., KAKAREKA S.V., TSYTIK P.V. Polychlorinated biphenyls in electrical equipment. Minsk: Minsk tipproekt, 28, **2003** [In Russian].
- DJUMAEV I.A., PECHENYUK O.I., ILYAZOV M.K., Management of polychlorinated biphenyls in the Kyrgyz Republic. Collection of articles, Bishkek, 256, **2011** [In Russian].
- KAKAREKA S.V., KUKHARCHIK T.I. Sources of persistent organic pollutants entering the environment: experience of identification and study. Nature Management. **22**, 157, **2012** [In Russian].
- LIU J., TAN Y., SONG E., SONG Y. A critical review of polychlorinated biphenyls metabolism, metabolites, and their correlation with oxidative stress. Chemical Research in Toxicology. **33** (8), 2022, **2020**.
- RAO U.M., FOFANA I., JAYA T., RODRIGUEZ-CELIS E.M., JALBERT J., PICHER P. Alternative dielectric fluids for transformer insulation system: Progress, challenges, and future prospects. IEEE Access. **7**, 184552, **2019**.
- DUPONT NOMEX, USA. Available online: https://www.matweb.com/search/datasheet_print.aspx?matguid=708a229bb73441b9a9ebc38ad3e44725, (01.12.2024) **2024**.
- Materials “Trihal”. Schneider Electric Company, France. Available online: <https://www.se.com/il/en/product-range/977-trihal/#overview>, (01.12.2024) **2024**.
- Dielectric Fluid | Liquid Cooling Solutions For Electrics. Acota, United Kingdom. Available online: <https://www.acota.co.uk/applications/dielectric-fluid>, (01.12.2024) **2024**.
- MIDEL ester transformer dielectric fluids Available online: <https://www.midel.com/midel-range/midel-7131>, (01.12.2024) **2024**.
- TLHABOLOGO B.A., SAMIKANNU R., MOSALAOSI M. Alternative liquid dielectrics in power transformer insulation: a review. Indonesian Journal of Electrical Engineering and Computer Science. **23** (3), 1761, **2021**.
- KULIKOVA T.V., MAIOROVA A.V., ILYINYKH N.I., BYKOV V.A. Formation of chlorine-containing components during high-temperature heating of polychlorinated biphenyls. Industrial Journal Konversiya. **45**, 74, **2008** [In Russian].
- MAIOROVA A.V., KULIKOVA T.V., SAFRONOV A.P., GORBUNOVA T.I., PERVOVA M.G., SHUNYAEV K.Y. Thermal Decomposition of Polychlorobiphenyls and Their Derivatives. Russian Journal of Applied Chemistry. **93**, 1254, **2020** [In Russian].
- SRIVASTVA U., MALHOTRA R.K., KAUSHIK S.C. Experimental investigation of convective heat transfer properties of synthetic fluid. Journal of Thermal Analysis

- and Calorimetry. **132**, 709, **2018**.
14. SAMBAEVA D.A., MAIMEKOV T.Z., KEMELOV K.A., IZAKOV ZH.B., MOLDOBAEV M.B., SHAIKIEVA N.T., MAIMEKOV Z.K. Sovol pyrolysis and chlorine decontamination of organic molecules based on metal oxides. *Ecology of Urbanized Territories*. **3**, 20, **2021** [In Russian].
 15. MESHALKIN V.P. Current Theoretical and Applied Research on Energy- and Resource-Saving Highly Reliable Chemical Process Systems Engineering. *Theoretical Foundations of Chemical Engineering*. **55** (4), 563, **2021**.
 16. MAIOROVA A.V., SAFRONOV A. P., KULIKOVA T.V., GORBUNOVA T. I., PERVOVA M. G., SHUNYAEV K.Y. Synthesis and thermal decomposition of alkoxy- hydroxy-derivatives of Sovol polychlorobiphenyls technical mixture. *Journal of Material Cycles and Waste Management*. **22**, 1552, **2020**.
 17. TIWARI R., AGRAWAL P.S., BELKHODE P.N., RUATPUIA J.V., ROKHUM S.L. Hazardous effects of waste transformer oil and its prevention: A review. *Next Sustainability*. **3**, 100026, **2024**.
 18. MONTANO L., PIRONTI C., PINTO G., RICCIARDI M., BUONO A., BROGNA C., MOTTA O. Polychlorinated biphenyls (PCBs) in the environment: occupational and exposure events, effects on human health and fertility. *Toxics*. **10** (7), 365, **2022**.
 19. WANG B., WU A., LI X., L., SUN C., SHEN Z., CHI Z. Progress in fundamental research on thermal desorption remediation of organic compound-contaminated soil. *Waste Disposal and Sustainable Energy*. **3**, 83, **2021**.
 20. IMASAKA Y., KATAYAMA Y., HARADA H., SIMION C., SIMION A.M., MITOMA Y. Dry dechlorination of polychlorinated biphenyls in contaminated soil by using nano-sized composite of metallic Ca/CaO and its mechanism. *Chemosphere*. **311**, 137197, **2023**.
 21. FAN G., LIU X., LI X., LIN C., HE M., OUYANG W. Mechanochemical treatment with CaO-activated PDS of HCB contaminated soils. *Chemosphere*. **257**, 127207, **2020**.
 22. HASHMI M.Z., KALEEM M., FAROOQ U., SU X., CHAKRABORTY P., REHMAN S.U. Chemical remediation and advanced oxidation process of polychlorinated biphenyls in contaminated soils: a review. *Environmental Science and Pollution Research*. **29** (16), 22930, **2022**.
 23. HUANG C., ZENG Y., LUO X., REN Z., TIAN Y., MAI B. Comprehensive exploration of the ultraviolet degradation of polychlorinated biphenyls in different media. *Science of the Total Environment*. **755**, 142590, **2021**.
 24. HU J., FENG Z., HUANG Z., YU J., LIU J. Mechanochemical destruction of 4-Bromochlorobenzene with CaO. Efficiency, kinetics, and mechanism. *Environment Protection Engineering*. **46** (2), 63, **2020**.
 25. ZHANG Z., ZHOU Z., LIU X., ZHANG H., XU H., LIN C., OUYANG W. Mechanochemical remediation of lindane-contaminated soils assisted by CaO: Performance, mechanism and overall assessment. *Journal of Hazardous Materials*. **458**, 131985, **2023**.
 26. WANG X., LV J., YING Y., MA Y., WU A., LIN X., YAN J. A new insight into the CaO-induced inhibition pathways on PCDD/F formation: Metal passivation, dechlorination and hydroxide substitution. *Science of the Total Environment*. **885**, 163782, **2023**.
 27. MAYMEKOV Z.K., SAMBAEVA D.A., IZAKOV Z.B., KEMELOV K.A., MOLDOBAEV M.B. Destruction of waste electrical insulating fluids of transformers in the environment: magnesium oxide-water-oxygen. *Problemy Regionalnoj Ekologii*. (4), 88, **2017**. [In Russian].
 28. RYZHENKO N.O., BONDAR O.I., CHETVERYKOV V.V., FEDORENKO Y.O. Polychlorinated biphenyls: Hazardous properties and environmentally sound management in Ukraine. *Regulatory Mechanisms in Biosystems*. **11** (1), 37, **2020** [In Russian].
 29. WU C., AWASTHI A.K., QIN W., LIU W., YANG C. Recycling value materials from waste PCBs focus on electronic components: technologies, obstruction and prospects. *Journal of Environmental Chemical Engineering*. **10** (5), 108516, **2022**.
 30. ZHU M., YUAN Y., YIN H., GUO Z., WEI X., QI X., DANG Z. Environmental contamination and human exposure of polychlorinated biphenyls (PCBs) in China: A review. *Science of the Total Environment*. **805**, 150270, **2022**.
 31. VELAZCO M.Z., PEDROSO P.G., RAMOS G.V., VAN LANGENHOVE H. Chemical dechlorination for the treatment of PCBs present in transformer oil (Sovtol-10): parameter study. *Afinidad*. **70** (563), **2013**.
 32. LIU Z.K. Computational thermodynamics and its applications. *Acta Materialia*. **200**, 745, **2020**.
 33. BELOV G.V., TRUSOV B.G., Thermodynamic modeling of chemically reacting systems. Moscow State Technical University Named After N.E. Bauman, Moscow, pp. 154, **2013** [In Russian].
 34. MAIMEKOV Z.K. Decomposition of spent polychlorinated biphenyls in a gas-liquid medium with the participation of barium, aluminum and calcium + magnesium oxides. Scientific project of the Ministry of Education and Science of the Kyrgyz Republic - state reg. No. 0007669-Bishkek, pp. 96, **2021** [In Russian].
 35. ZAITSAU D.H., EMELYANENKO V.N., PIMERZIN A.A., VEREVKIN S.P. Benchmark properties of biphenyl as a liquid organic hydrogen carrier: Evaluation of thermochemical data with complementary experimental and computational methods. *The Journal of Chemical Thermodynamics*. **122**, 1, **2018**.
 36. MAIMEKOV T.Z., SAMBAEVA D.A., MOLDOBAEV M.B., BAZHIROV T.S., MAIMEKOV Z.K. Forecasting and evaluation possibilities carbon footprint during combustion of fuel oil in medium and low power boilers. *Theoretical Foundations of Chemical Technology*. **57** (5), 898, **2023**.
 37. MAIMEKOV Z.K. Scientific basis for optimization of liquid fuel combustion processes and recarbonization of water-salt systems. Ministry of Education and Science of Kyrgyz Republic, Bishkek, pp. 410, **2015** [In Russian].
 38. On approval of methods for quantitative determination of greenhouse gas emissions and greenhouse gas absorption, 2022, Russian Federation. Available online: <http://publication.pravo.gov.ru/Document/View/0001202207290034>. (01.12.2024) **2022**.
 39. DUROJAYE O., LASEINDE T., OLUWAFEMI I. A descriptive review of carbon footprint. *Advances in Intelligent Systems and Computing*. In book: *Human Systems Engineering and Design II*, pp. 960, **2020**.
 40. BÖHRINGER C., FISCHER C., ROSENDAHL K.E., RUTHERFORD T.F. Potential impacts and challenges of border carbon adjustments. *Nature Climate Change*. **12** (1), 22, **2022**.