Study Biochar In Plugging Of Oil And Gas Wells (CO HB 23-1069)

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The following document has been prepared in accordance with Colorado house bill 23-1069 to provide recommendations for the development of a pilot program to study the use of biochar in the plugging of oil and gas wells.

Table of Contents

Motivation	4
Background	4
Oil and gas well decommissioning	4
Oil and gas wells in Colorado	5
Plug and Abandonment (P&A) of oil and gas wells	
Biochar use in capping abandoned oil gas wells	
Research Tasks	8
Task (3)(a)(I)	8
Plain Language Summary	8
Biochar feedstocks and characteristics	8
Biochar production conditions	<u></u>
Biochar as a means of reducing GHG emissions and sequestering carbon	10
Gaseous emissions and mitigation strategies	11
Net Greenhouse Gas Emissions Associated with Biochar	12
Influence of biochar on cement performance	
Compressive strength	
Tensile Strength	
Flexural strength	
Flow Rate	
Chloride-ion penetration	
Sulfate attack	
Biochar as a gas adsorbent	
Carbon dioxide	16
Methane	
Other gaseous emissions	17
Summary and Recommendations	

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Task (3)(a)(II)	19
Plain Language Summary	
Methodology	19
Regulations for O&G well plugging	19
Biochar and other supplementary cementitious materials	
Summary and Recommendations	20
Task (3)(a)(III)	21
Plain Language Summary	21
Methodology	21
Results and discussion	21
Summary and Recommendations	
Task (3)(a)(IV)	24
Plain Language Summary	24
Methods	24
Biochar Characterization	24
Biochar-cement composites	25
Results	27
Biochar pH	27
Biochar size	
Biochar/cement surface area and porosity	
Biochar water holding capacity	
Cement slurry viscosity	
Biochar as a cement additive	
Chloride and Sulfate Sorption	
Summary and Recommendations	34
Task (3)(a)(V)	36
Task (3)(a)(VI)	37
Plain Language Summary	37
Methodology	37
Results and Discussion	38
Summary and Recommendations	39
Task (3)(a)(VII)	40
Plain Language Summary	40
Methodology	40
Overview of Forest Inventory Analysis	
County, ownership, and forest type	41
Analysis	42
Results and Discussion	45

Limitations	45
Task (3)(a)(VIII)	46
Plain Language Summary	46
Methodology	46
Results and Discussion	48
Summary	Error! Bookmark not defined.
Task (3)(a)(IX)	52
Plain Language Summary	52
Using biochar for carbon credits or offset	52
Compliance with existing legislation	53
Conclusions and Future Recommendations	54
References	57
Appendix A	69
Appendix B	73
Appendix C	79
Appendix D	80
Annendix F	82

Motivation

Background

Since the mid-1800s, more than 4 million oil and gas wells have been drilled in the United States. As of 2018, approximately 2.1 million wells are no longer being used for production, injection, or other purposes, but also have not been plugged [1]. Many such wells have been abandoned, as the financial assurance requirements are often too low to cover the costs associated with decommissioning [2], an extended process that ends with permanent plug and abandonment (P&A) of wells which are no longer in use.

Oil and gas well decommissioning

Decommissioning oil and gas wells is an extensive process, which includes an assessment of the well's physical condition, identification of potential leaks or hazards, cleaning the wellbore, removing surface equipment, and restoring the surrounding well pad. Specific considerations for decommissioning include possible risks during and after facility removal, intended methods and strategies for decommissioning, additional analyses needed, operations plans, impacts on adjacent fields and facilities, waste control, and monitoring for future pollution [3]. Associated risk factors include high temperatures, unconsolidated formations, changes in formation strength after depletion, uncertainty in reservoir pressure predictions, formation permeability, tectonic stress, casing pressure, and others [3]. Therefore, well plugging and abandonment can be a costly endeavor. Out of 19,500 wells surveyed in the United States, the median well plugging cost was approximately \$20,000, and plugging plus surface reclamation was over \$76,0001 [2], well exceeding the approximately \$2,122 ensured per well by Bureau of Land Management Bonds² [4]. In the event that companies are unable to properly plug oil and gas wells, the wells become "orphan wells", effectively wards of the state. Structural decline in oil and gas demand may increase the number of orphaned wells, further pushing the cost of plug and abandonment onto the taxpayer.

Despite the high costs associated with oil and gas well decommissioning, it is important that inactive wells are plugged from both a human and environmental health perspective. Unplugged wells are associated with the migration of gases and fluids from cement and steel degradation, leading to contamination of surface and groundwaters [2]. Additional risks associated with unplugged wells include large methane (CH₄) emissions [5], as well as emission of carcinogens such as benzene and other volatile organic carbons, although this exposure pathway is not well understood [6, 7]. On average, each unplugged well emits 0.13 t CH₄ per year, representing ~2.6% of total U.S. energy methane emissions [1]. Published emissions data from 412 plugged and 427 unplugged wells in the U.S. and Canada indicate that on average 1.6 g CH₄/h are emitted by plugged wells, with the largest emissions associated with wells in Oklahoma, Ontario, and Pennsylvania. Unplugged wells have much higher methane emissions (7.5 g CH₄/h), with the largest emissions in Ohio, Pennsylvania, and California [8, 9]. From this data, we can conclude that emissions vary across well types, geology, and plugging status.

¹ Data published 2021

² As of May 2018

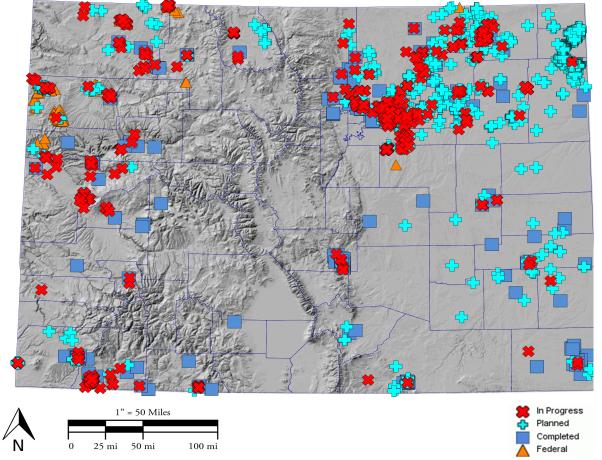


Figure 1. Map of orphaned wells in Colorado created on the ECMC GIS Online (https://cogccmap.state.co.us/cogcc gis online/)3. Counties are designated by blue lines and topography are in grey. Red crosses indicate wells where work has not yet begun, and no funds have been expended. Blue crosses indicate wells where work has begun at the site, but reclamation is not yet complete. Blue squares represent sites where work has been completed and the site has passed its final reclamation. Orange triangles represent sites where a federal agency is or will be responsible for some or all work at the site.

Oil and gas wells in Colorado

Colorado is the fifth-largest crude oil-producing state in the United States [10], with over 53,000 active oil and gas wells [11]. Oil and gas production in the state is centered around the Denver-Julesburg (DJ) basin in northeastern Colorado and southeastern Wyoming, which accounts for almost 90% of Colorado crude oil production [10]. As of 2023, there are approximately 33,000 unplugged and abandoned wells and 49,000 plugged and abandoned wells in Colorado [12] (Figure 1). Methane emissions for 334 Colorado wells (128 plugged and 206 unplugged) were recently investigated, and the authors found that plugging remains effective for at least 50 years after the well is sealed and covered with soil. Of the unplugged wells, 61% were emitting methane, and the average methane emission was over 70x the national average [8, 9, 13]. The authors concluded that most methane emissions result from recent failures in management decisions (such as lack of routine maintenance and service of operating marginal wells), rather than neglect and decay of plugged oil and gas wells, as no plugged wells in the study

³ Date accessed: 10 May 2024

were observed to be emitting CH₄. Therefore, newly abandoned wells represent a greater risk than historic wells and should be an operational focus [14].

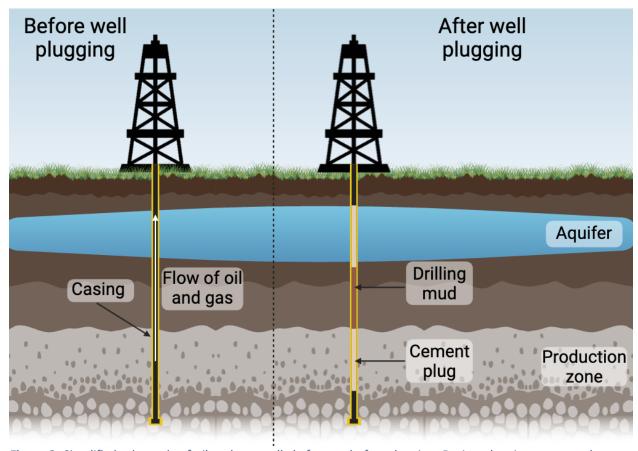


Figure 2. Simplified schematic of oil and gas wells before and after plugging. During plugging, cement plugs are placed in the wells and drilling mud is placed in the spaces between. Successfully plugging a well will negate movement of oil and gas from the production zone to the soil surface.

Plug and Abandonment (P&A) of oil and gas wells

During well plugging, several cement plugs are placed in the wellbore to isolate the reservoir and other fluid-bearing formations (**Figure 2**). Well plugging criteria indicates that a good well barrier material must provide long-term integrity, be impermeable and unshrinking, withstand mechanical loads, and be resistant to a variety of chemical substances. Portland cement is the most commonly used well plugging material, mainly comprised of CaO, SiO₂, Al₂O₃, and Fe₂O₃ [15]. Although well integrity must be ensured after abandonment, old, plugged, and abandoned wells are prone to leaking [16-18]. The primary cause of leakage in plugged wells is the formation of microannuli and radial cracks, which may form in the cement sheath during normal well operations such as pressure testing, injection simulation, and production [19-21]. Leakages may permeate through the cement plug or through the cement-casing interface; therefore, a cement plug on its own is not always sufficient to prevent leakage from the well after abandonment, especially in older wells [15].

Biochar use in plugging abandoned oil and gas wells

To improve cement integrity, and therefore reduce the risk of greenhouse gas and fluid leaks from plugged oil and gas wells, cement additives have been explored. Specifically biochar, a carbon-rich material produced by pyrolysis, has received attention because the materials needed to create biochar are highly abundant and it is relatively cheap to make. Additionally, studies show that biochar can improve mechanical strength in some cement composites and therefore increase the lifetime of plugging operations [22]. Biochar may also be able to offset some of the carbon dioxide (CO₂) created during cement production by indefinitely sequestering large amounts of carbon which can no longer be mineralized to CO₂. Therefore, we evaluated the feasibility of biochar-cement composites for oil and gas well plugging operations and conducted technoeconomic analyses to determine the associated cost (**Figure 3**).

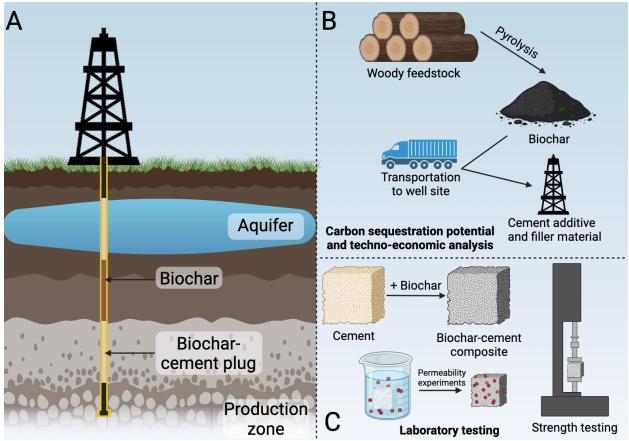


Figure 3. Conceptual figure for the HB-1069 report. Panel A depicts the intended biochar uses in oil and gas well plugging, including the use of biochar as a filler material and as a cement additive. Panel B depicts some of the considerations for the carbon sequestration potential and costs associated with biochar production and transportation. Panel C illustrates the laboratory testing necessary to determine whether mixing biochar with cement retains the same strength and durability as pure cement.

Research Tasks

The following sections address the individual tasks stated in CO HB 23-1069.

Task (3)(a)(1)

Review peer-reviewed scientific articles and studies on biochar's capacity to:

- (A) Lower greenhouse gas emissions;
- (B) Lower chemical leaks;
- (C) Remove and sequester carbon;
- (D) Lower the carbon footprint in cement;
- (E) Add strength to cement; and
- (F) Bind chemicals such as methane, benzene, and carbon dioxide from fugitive emissions

Plain Language Summary

Biochar is a carbon-rich material which can be made from a wide variety of starting materials that influence the final product. Specific considerations for biochar production include starting material (feedstock), heat, and the amount of time temperatures are held for. Due to the high number of variables which can influence the final biochar product, special consideration must be taken to ensure the right biochar is chosen for the intended application. Woody biomass has emerged as a promising biochar material for oil and gas applications due to its high carbon content and residence time, which make it a good candidate for carbon sequestration (meaning that carbon can be trapped within the biochar itself and does not contribute to carbon dioxide formation), and that it has good gas sorption properties (meaning that gaseous particles are able to be attached to the biochar surface).

We reviewed three primary biochar applications for use in the oil and gas well decommissioning process: 1) biochar as a cement additive, 2) biochar as a gas sorbent, and 3) biochar as a means of sequestering carbon to offset CO₂ emissions (Figure 3). To address the first and second application, we reviewed literature associated with biochar-cement composites to evaluate the effects of biochar on cement strength (including compressive, tensile, and flexural), flow rate of the cement paste, chloride-ion penetration, and sulfate attack. For the third application, we synthesized literature findings related to the sorption of gaseous emissions such as carbon dioxide and methane. The results of the literature review indicated that biochar is a promising additive for cement mixtures, but that starting material, heating time, and particle size may influence the final product, with mixed results. Biochar is also a promising material for sorption of gaseous emissions, although many studies are conducted in controlled laboratory settings creating uncertainty in how well the results can be applied in a field setting, in which biochar will be submerged in water or incorporated into cement. Overall, current literature indicates that biochar has the potential to lower greenhouse gas (GHG) emissions through gas sorption and sequester carbon in cement, mitigate leaks such as methane in oil and gas wells, and could potentially add strength to cement under some conditions.

Biochar feedstocks and characteristics

Biochar is a solid, carbon-rich material produced during pyrolysis (heating of an organic material in an oxygen-depleted atmosphere) across a range of ~250-900 °C [23]. Biochar can be

distinguished from other sorbents by high availability of feedstock, low cost of production, and high potential adsorption capacity for contaminants [24]. Among the characteristics that make biochar a good sorbent are high pore volume and surface area, high organic carbon content, and high cation-exchange capacity, which confer the ability to stabilize both organic and mineral compounds in complex matrices such as soil and water [25, 26]. Recently, biochar has attracted considerable attention for its ability to mitigate atmospheric CO₂ to aid in sustainable environmental remediation as a cost-effective negative emission technology (NET) [27, 28].

Many reviews exist detailing biochar production, properties, and applications, as biochar is affected by processing conditions, feedstock, and post-pyrolysis modifications, which can be tailored for different application requirements [26, 29-39]. Many feedstocks have been used to produce biochar, and can be divided into four major categories: 1) woody biomasses originating from tree species, 2) herbaceous biomasses derived from agricultural residues, 3) biosolid sludge from wastewater treatment, and 4) animal and human waste, including manure and food waste [38]. Analyses of the four major types of biochar indicate that the physical and chemical properties of biochars from woody biomass, herbaceous biomass, and animal and human waste are similar, but wastewater sludge is not [40]. Of the four major feedstock categories, biochars derived from woody biomass tend to have the highest surface area [41], and therefore the highest potential adsorption capacity.

Biochar production conditions

In addition to feedstock, pyrolysis temperature and residence time can have significant impacts on biochar properties. Increases in pyrolysis temperature typically yield biochar with larger pore sizes and higher specific surface areas [42]; however, biochar yield decreases as temperature increases [38], with concurrent increases in the yield of gaseous and liquid products [43, 44]. Pyrolysis temperature also influences biochar pH, which is positively correlated with the contents of total base cations and carbonates [38], which may influence how pollutants interact with the biochar surface. Pyrolysis can be divided into two main categories: slow and fast pyrolysis. Slow pyrolysis generally ranges from 350-900 °C with a temperature ramp from 0.5-20 °C/min and a residence time⁴ of minutes to days. Fast pyrolysis ranges from 500-700 °C with a temperature ramp of 10-200 °C/s and a residence time of 0.5-10 seconds. While fast pyrolysis takes significantly less time, slow pyrolysis can yield over 2x the biochar produced [38]. Slow pyrolysis also increases the specific surface area of biochar, which is further influenced by production temperature, and may increase adsorption capacity [45, 46]. The ideal pyrolysis temperature range for biochar production falls between 450 and 600°C [36]. In contrast, biomass gasification is a high temperature thermochemical conversion method for biomass that falls between 600 and 1000°C, although the main product is syngas with small amounts of biochar and bio-oils produced [47].

Within slow pyrolysis, different reactor technologies and configurations exist, mainly defined as how they move material through the pyrolysis design. A 2023 Global Biochar Market Report by the United States Biochar Initiative (USBI) and International Biochar Initiative (IBI) found that five technologies comprise 82% of the biochar production methods: 1) stationary

9

⁴ Amount of time a specific temperature is held

system via injection auger, 2) stationary system via rotary kiln, 3) stationary system via batch reactor, 4) portable retort, and 5) mobile carbonizer [48]. The auger reactor is a common design comprised of a stationary steel outer tube with an auger that moves material forward as it rotates. The advantages of this production method include a lower operating temperature and smaller reactor sizes [49]. The rotary kiln is a widely used design consisting of a heated rotating steel cylinder that can handle a wide range of biomass feedstocks [50]. Its design ensures better mixing of biomass, longer residence times, and enhanced heat exchange for pyrolysis reactions [51]. Batch reactors have a simpler design and operation compared to augers and rotary kilns, although the start-stop nature of the reactor can lead to higher energy consumption per unit biochar produced [52]. Mobile carbonizers and portable retorts can be used on-site allowing for quick adaptation to different biomass sources and can typically handle higher moisture contents than stationary systems [53]. On-site production reduces GHG emissions associated with transporting feedstock but may require diesel generators in areas without grid connection, which can lead to a trade-off in emissions.

Biochar as a means of reducing GHG emissions and sequestering carbon

Biochar is widely used across various industries for applications such as agricultural soil amendments, environmental remediation, and carbon storage in soil [40-47]. Each application requires specific biochar properties to maximize effectiveness. For long-term carbon sequestration using biochar, carbon must be removed from the short-term carbon cycle and stored long-term, most often in the soil [24]. The effectiveness of carbon sequestration through biochar depends on the yield of biochar from the initial feedstock, the amount of stable carbon in the biochar, and its long-term stability under environmental conditions [48-50]. Both production conditions and feedstock properties influence the amount of stable carbon in biochar [51-53], with higher pyrolysis temperatures and longer residence times associated with greater carbon sequestration potential [27, 52].

The stable carbon content of biochar can range from 50% to 85%, depending on the thermochemical conversion conditions (i.e., heating rate, temperature, and reactor configurations) [54] and feedstock type [55]. For instance, biochar made from hardwoods may have different pore structures and mineral content compared to biochar made from grass or manure, leading to variations in carbon dynamics. Higher lignin contents in the initial feedstock generally yield more stable biochars [27], making woody feedstocks excellent candidates for carbon sequestration applications. Captured carbon in biochar can remain stable for centuries, effectively removing it from the rapid-turnover carbon cycle and aiding in reducing carbon in the atmosphere [56, 57].

The choice of feedstock biomass not only affects the efficiency of the pyrolysis process but also the overall life cycle emissions of the biochar system. Using waste materials, such as forestry residues, minimizes the carbon footprint compared to dedicated energy crops, which may require additional inputs (i.e., fertilizers, land use changes) that can offset some of the GHG benefits in the produced biochar [58]. This approach also enhances the sustainability of the biochar system by reducing additional carbon emissions associated with biomass cultivation and processing [59].

Lignocellulosic materials, such as wood and agricultural residues, are particularly effective in producing high-quality biochar with substantial carbon retention properties [60]. However, woody materials contain fewer extractives (e.g., sugars and metabolites) and more lignin than leafy, herbaceous materials, making them richer in carbon [23]. Forest residues generally have minimal additional negative environmental impacts, but their availability is limited and there can be competition for their use, as they can also serve other purposes [23]. Therefore, careful selection of feedstock materials is crucial for carbon sequestration purposes.

Gaseous emissions and mitigation strategies

Among the most common GHG emissions during oil and gas production are methane, (CH₄), hydrogen sulfide (H₂S) and carbon dioxide (CO₂), which contribute to climate change and represent a health safety risk [54]. Other problematic emissions associated with oil and gas production include light hydrocarbons, gaseous nitrogen forms, other sulfur compounds, polycyclic aromatic hydrocarbons, and small amounts of mercury [55]. One method to minimize emissions is to use a sorbent to bind gas particles. A good sorbent must have a high adsorption capacity, low friction flow, withstand high temperatures, have fast adsorption kinetics, and be stable in oxidizing or reducing environments [24]. Activated carbons have emerged as excellent sorbents for the removal of contaminants due to their large internal surface area and large pore volumes. However, the high cost associated with activated carbon production limits the feasibility of their use [24]. To combat high costs, biochar has emerged as an environmentally sustainable and cost-effective alternative to activated carbon for sorption of gaseous emissions.

In addition to the GHG emissions associated with oil and gas production, activities related to the cement life cycle (e.g., mining, processing, and transport of raw materials) are associated with a large environmental impact. Portland cement production creates 0.98 tonnes of carbon per tonne of cement [56] and contributes ~6-7% of total global CO₂ emissions [57-60]. To offset GHG emissions, CO₂ sorbents have been suggested to enhance carbon sequestration in cementitious composites. The large surface area and high water absorption capacity of biochar make it a good cement additive [39], which is also ~10x cheaper than other CO₂ adsorbents such as activated carbons [61]. To that end, the possibility of using biochar to develop low-carbon or carbon-negative concretes has been thoroughly investigated [14, 39, 62, 63], and suggests that biochar could offset the large GHG emissions associated with cement production. A study on cement mortars indicates that biochar could improve carbon-capturing capacity up to 12% with a 4% biochar weight replacement [64]. Another study found that a 5% weight replacement can result in a 15% decrease in GHG emissions when the GHGs from all concrete mixture materials are considered, suggesting that using biochar in concrete products could be an avenue towards low-carbon concrete design [65, 66]. The carbon stored within cement would no longer be sequestered once the cement is disposed of, destroyed, or decomposed [67]. When used in operations such as well plugging, biochar is expected to maintain all its carbon for at least 100 years [68]. However, long-term durability studies are limited, and the mechanism of carbon capture is still unknown.

Research indicates that biochar could act in a dual capacity to improve carbon sequestration and enhance the strength of cement mortars through accelerated hydration and internal curing [69]. The incorporation of biochar particles into the cement matrix could absorb cracking energy in cementitious composites and increase tortuosity in the breaking path, increasing cement

strength compared to non-amended cements [70-74]. The presence of fixed carbon and the low amount of reactive groups inside the biochar makes it unlikely to cause chemical decay in the internal structure of the cement [61], potentially increasing cement longevity.

Net Greenhouse Gas Emissions Associated with Biochar

Several life cycle assessments (LCA) and GHG mitigation assessments have looked at the production of biochar from the thermochemical conversion of different biomass feedstocks. These studies take into account GHG emissions related to feedstock sourcing, biochar production, and the stable carbon [75]. A wide range of values exist due to different assumptions in the LCA studies, such as type of feedstock, difference in technology (pyrolysis type and product yield), operating conditions (e.g., temperature, heating rate), and LCA model boundaries or decisions, source of energy, and methodological differences. Biochar production literature regarding GHG emissions indicates that out of the main life cycle stages (biomass transportation to production facility, pre-processing of biomass, thermochemical conversion, transportation of biochar to end consumer), the stage with the greatest environmental GHG impact is the thermoconversion process [76]. The drying process is usually also a significant factor in biomass supply chains due to the energy inputs needed to evaporate moisture from the biomass. Considering only biochar produced from wood-based resources, **Table** 1 illustrates the potential estimates of negative emissions from relevant literature including both the GHG emissions associated with biochar production along with the GHG reductions.

Table 1: Net Greenhouse Gas (GHG) emissions associated with biochar produced from various types of woody biomass. This includes the sequestered carbon in biochar along with the emissions associated with the biochar production process.

Biochar Feedstock	Pyrolysis Conditions	Net GHG Emissions (t CO₂e/t biochar)	Reference
Cardboard	Slow Pyrolysis	-1.5	(Ibarrola et al. 2012)
Wood Waste	Slow pyrolysis	-1.2	(Ibarrola et al. 2012)
Sawmill residues	Slow pyrolysis	-1.7	(Hammond et al. 2011)
Forestry Residue Chips	Slow pyrolysis	-1.9	(Hammond et al. 2011)
Small round wood	Slow pyrolysis	-1.7	(Hammond et al. 2011)
Short rotation forestry	Slow pyrolysis	-1.6	(Hammond et al. 2011)
Canadian forestry residue chips	Slow pyrolysis	-1.4	(Hammond et al. 2011)
Short Rotation Coppice	Slow Pyrolysis	-1.6	Hammond et al. 2011
Conifer Tree	Gasification	-(1.7 - 2.3)	(Lugato et al, 2013)
Wood pellets	Slow pyrolysis	-1.9	(Homagain et al. 2015)

Biochar represents a noteworthy carbon sequestration technique due to its capacity for waste reduction and GHG mitigation. It differs from solely afforestation or direct air capture by capitalizing on waste biomass and converting it into a stable carbon form. Moreover, biochar production is economically viable and scalable compared to other sequestration methods [77]. By focusing on the substantial stable carbon content within biochar, its effectiveness in contributing to long-term carbon management strategies becomes evident, underscoring its crucial role in not only reducing GHG emissions but also providing a durable solution for carbon sequestration.

To effectively use biochar as a tool for mitigating climate change and reducing CO₂ levels, large quantities of biochar would need to be applied to the environment [78]. Several studies have calculated the total net emissions of biomass pyrolysis with biochar. Roberts et al. calculated the total emissions abatement of biomass pyrolysis with biochar applied to soil is between 2.6 and 16 tonnes CO₂e per tonne of biochar [77]. The amount of emissions abatement depends on the feedstock, its conventional management practice, fossil fuel substitution, and the cropland to which biochar is applied [77]. Other studies have concluded that these systems can mitigate 0.7–1.4 Mg CO₂e per Mg of feedstock consumed [75]. Another study by Yu et al. found that when biochar is produced from pyrolysis, the net global warming potential (GWP) ranges from -442 to -1570 kg CO₂e per dry tonne [79]. Amonette et al. reported that LCAs indicate that biochar offsets GHG emissions by about 0.4-1.2 tons of CO₂e per ton of dry feedstock [50]. The variations in emission offsets can be attributed to differences in thermochemical conversion methods, feedstock types, operating conditions, and LCA system boundaries and assumptions.

Influence of biochar on cement performance

Biochar-cement composites have been studied to determine the influence of biochar on cement strength and characteristics (**Figure 4**). While feedstock, pyrolysis temperature, particle size, and % replacement varied across studies, important observations can still be made. The papers reviewed are summarized in **Table A** and described below.

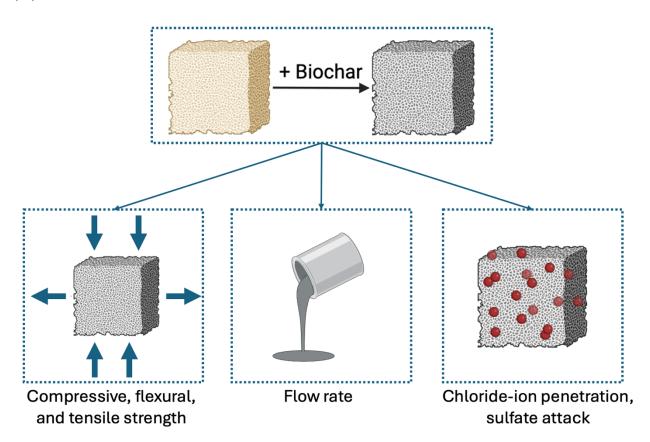


Figure 4. Cement characteristics which may be influenced by the addition of biochar to the paste. Compressive, tensile, and flexural strength may increase or decrease depending on the amount and type of biochar added. Flow

rate typically increases but can be comparable to the flow rate of non-amended cement with the addition of superplasticizers. It is likely that biochar improves cement resistant to chloride-ion penetration and sulfate attack, but more research is needed to determine the role of biochar in cement-ion interactions.

Compressive strength

One of the most important values for biochar-cement composites is compressive strength, which indicates the capacity of a material or structure to withstand loads. Overall, compressive strength improvements are highly variable depending on the feedstock: On the lower end, weedtree feedstock improved compressive strength by 3.4% at a 2 weight % replacement⁵ [80], and rice husk only slightly improved compressive strength in another study [81]. Small weight % replacements also resulted in increased compressive strength for biochars made from wood saw dust [82], coconut and mixed tropical wood [64, 69], and olive stone, rice husks and wood chips [83]. Moderate improvements (4-7%) were reported from dewatered sludge [84], sugarcane bagasse [85], and waste synthetic eucalyptus plywood [86]. On the higher end, waste wood increased compressive strength by 8.4% at 2-3 weight % addition [87] and bamboo chips resulted in up to a 20% increase in compressive strength at 1 weight % replacement [88]. In a study comparing the compressive strength of biochar from bagasse and rice, peanut, wheat, and coconut husk, compressive strength was positively related with the amount of amorphous silica in the feedstock [63], although specific mechanisms for compressive strength changes are still being investigated. In general, a 1-2 weight % replacement resulted in the optimum increase in compressive strength, as the rate of strength improvement began to reduce when a higher dosage of biochar was added [22].

Tensile Strength

Tensile strength is a measure of how resistant the cement is to tension, or to being pulled apart. Tensile strength is either reduced or improved by biochar addition based on the feedstock. Sugarcane bagasse at 5-20 weight % replacement displayed a slight decrease in tensile strength at 5%, and tensile strength continued to decrease with further cement replacement [85]. Woody biomass biochar also resulted in decreased tensile strength with an increased dosage of biochar, and the optimal dosage (defined as highest increase in tensile strength) was determined to be approximately 1-2 weight % [89]. The tensile strength of cement and waste synthetic eucalyptus plywood slightly increased at 6.5 weight % replacement. Less than 1 weight % replacement of biochars made from rice husk and pulp paper mill sludge yielded similar tensile strength to unamended cement, indicating that low replacement may not have much of an effect on tensile strength [90]. Finally, wood sawdust yielded the largest increase in tensile strength changes. These studies suggest that compared to compressive strength, biochar has smaller effects on changing tensile strength.

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⁵ Biochar-cement studies often rely on two methods for biochar incorporation. Methods using "replacement" refer to studies that have substituted a certain weight % of cement for that amount of biochar (i.e., 3 weight % replacement indicates 3% of the cement has been replaced with and equal weight of biochar). In these studies, the amount of dry cement in the replicates containing biochar will contain less dry cement than the control. Methods using "addition" refer to studies that have added a certain weight % of biochar to a set amount of cement. In these studies, the controls and the biochar-cement composites will contain the same amount of dry cement.

Flexural strength

Flexural strength refers to a material's ability to resist deformation under load. Particle size is important for flexural strength changes in biochar-cement composites, as smaller particles are reported to yield better results [22]. Larger particle sizes (<500 um) of wood chip and desert palm rachis biochars (<500 um) slightly improved flexural strength at 1 weight % replacement [92, 93]. Decreasing the particle size to <200 um for wood chip biochar improved flexural strength up to 10% at 1.5 weight % replacement [94], and the same size woody biomass biochar showed a maximum flexural strength gain at 0.5% [89]. Meanwhile, rice husk waste biochar <300 um improved flexural strength by 5.8% at a 2 weight % replacement [81] and improved flexural strength by 13% when sieved to <30 um [95]. Finally, wood saw dust biochar <50 um added at 0-2 weight % had little effect on flexural strength [96]. Therefore, finer biochar particles are preferential for flexural strength improvements at replacements of 1-2 weight %, and may provide similar flexural strengths to biochar-free cement at higher replacements [22].

Flow Rate

Flow rate is important for the workability of cement and is influenced by free water in the biochar-cement mixture. Overall, biochar reduces flow rate, increasing viscosity. Flow reduction for biochar made from wood chips, saw dust, and rice husk was reported to be between 8-13%, and the amount of flow reduction is correlated to the amount of cement replaced by biochar [63, 92, 97, 98]. 5% weight replacement is reported to be ideal, although the use of plasticizers can improve flow [92].

Chloride-ion penetration

Chloride-ion penetration is the depth to which chloride ions penetrate into the concrete, which may cause corrosion and decrease durability. Studies focusing on chloride-ion penetration are limited in comparison to strength tests; nevertheless, high salt concentrations in geological formation waters underscore the need for further investigation into the role of biochar in cemention interactions. A study on rice husk and wood waste biochars found that there was a 120-day strength loss from chloride-ion penetration at weight replacements of 0-2% [99]. However, another study on rice husk biochar indicated that chloride-ion diffusion was reduced, and that less strength was lost at a 5 weight % replacement [100]. A separate study on wood waste biochar spanning 0-10 weight % replacement indicated that the chloride diffusion coefficient decreased by up to 32% at a 1-3 weight % replacement [101]. Given the inconsistencies in published results, more research is needed to determine the role of biochar on chloride-ion penetration in biocharcement composites. Refer to task (3)(a)(IV) to review the experimental design and results we gathered regarding the influence of biochar on chloride-ion penetration.

Sulfate attack

Sulfate attack is a process which is caused by salt crystallization and can lead to concrete expansion, cracking, strength loss, and disintegration. Like chloride-ion penetration, studies relating to sulfate attack are limited, though the results are more consistent. Sugarcane bagasse biochar at 5-10 weight % replacement indicates that a 5% replacement imbues higher strength against sulfate attacks at 56 and 90 days [102]. Rice husk and wood waste biochars reveal that

strength loss against sulfate attack was reduced at a 2 weight % replacement, and a higher silica content was found to provide better resistance to sulfate ion penetration [99]. Therefore, it is likely that other biochars will also improve cement resistance to sulfate attack. Refer to task (3)(a)(IV) to review the experimental design and results we gathered regarding the influence of biochar on sulfate attack.

Biochar as a gas adsorbent

In addition to the potential influences of biochar on cement performance, there has been extensive interest in the potential for biochar to adsorb various gaseous emissions from oil and gas production. Activated carbons have been used for carbon dioxide, methane, and other gaseous adsorption studies, and are highly effective but also very expensive at over \$6,000 per tonne. Therefore, biochar has emerged as a potential alternative sorbent.

Carbon dioxide

Biochars have been extensively researched to determine the amount of CO_2 which may be adsorbed. Pyrolysis temperature can influence adsorption capacity, as sugarcane bagasse and hickory wood pyrolyzed at 300-600 °C demonstrated that a higher temperature had a better CO_2 capture performance. Comparisons between functional groups of the two feedstocks showed that high surface area and the presence of nitrogenous groups also play a role in CO_2 adsorption [103]. Metals may also influence CO_2 adsorption, as determined by a study on date palm leaf biochar [104]. Finally, CO_2 adsorption is partly determined by feedstock, as indicated by a comparative study that found that the adsorption capacity of each biochar was in the order of perilla leaf > soybean stover > Korean oak > Japanese oak [105].

Activated biochars (AB) have been used for carbon dioxide adsorption across a variety of raw organic materials and may improve CO₂ sorption capacity compared to non-activated biochars. AB from palm kernel shell was able to adsorb 23.52 kg CO₂/t, indicating that palm shell biochar is viable for gas adsorption applications [106]. Novus pallet scrap AB prepared at various temperatures revealed that wood wastes pyrolyzed at 450 °C yielded better CO₂ sorbents compared to those manufactured at higher temperatures [107] and may be better sorbents than their non-activated counterparts.

Adsorption of CO₂ is also possible when biochars are incorporated into cement mixtures. Corn stover biochar-cement composites indicate that three-day CO₂ uptake can be enhanced by an optimal biochar dosage of 4-6%, and as little as a 2-3 weight % replacement can increase CO₂ uptake by 2-3% [108]. Biochar from tropical mixed wood saw dust was used to determine that there was a seven-day reduction in carbonate mineralization and that the CO₂-equivalents were 6-7% lower [64]. A study comparing 84 types of biochar made from various feedstocks indicated that biochar-cement composites resulted in overall negative CO₂ emissions, along with having a good adsorption capacity for pollutants [109], emphasizing a promising avenue for offsetting CO₂ emissions from the cement production process.

Methane

Methane is a powerful GHG, which has 28x more warming potential than carbon dioxide. A study on torrefied cardboard (main product was biochar) found that methane adsorption increased with torrefaction⁶ time and decreased with chemical treatment, indicating that a slower pyrolysis process may increase CH₄ adsorption capacity [110]. Black poplar-derived biochar studies indicate that a larger micropore volume results in higher CO₂ and CH₄ uptakes, although the biochar was selective towards CO₂ over CH₄ [111]. Preferential adsorption of CO₂ was also reported in another study, along with H₂S, over CH₄ due to sorption site competition [105].

Other gaseous emissions

H₂S and polycyclic aromatic hydrocarbons (PAHs) receive less attention in the literature but are still important for determining risk factors associated with abandoned oil and gas wells. Biochar mineral components are important for reacting with sulfur, as a comparative study found that the elemental composition of pig manure biochar contributed to a higher capacity of H₂S sorption in both dynamic and static systems over sewage sludge biochar [112]. Particle size and functional groups are also important for determining H₂S sorption capacity, as demonstrated by a study on camphor biochar. However, camphor pyrolyzed from 100-500 °C indicates that pyrolysis temperature is not a major determinant for H₂S sorption as all biochars were effective across the temperature range [113].

PAH sorption by biochar has been extensively studied in aqueous and soil matrices but is less well understood for gaseous emissions. However, a study on naphthalene and *m*-dinitrobenzene sorption to pine needle biochar created from 100-700 °C found that biochar surface functionalities were dependent on pyrolysis temperature, which played a role in the sorption of organics. Specifically, partitioning of PAHs was determined by surface porosity and steric hindrance, which resulted in preferential sorption of smaller organic molecules [45].

Summary and Recommendations

Collectively, the research reviewed here reveals interesting insights into the role of biochar on cement strength and oil and gas emissions mitigation. Data supports the use of biochar in reducing GHG emissions, although the specific reduction is highly dependent on the biochar feedstock and pyrolysis configuration. When incorporated in appropriate amounts, biochar may improve compressive, tensile, and flexural strength, and improve cement cracking resistance, although too much biochar (amount varies by system) may decrease cement strength. The role of biochar on sulfate attack and chloride-ion penetration remains unclear, although small weight % incorporations may yield positive results. Results indicate that up to 5 weight % replacement of biochar could be used for sustainable concrete design, but more research is needed to fully understand the drivers of mechanical strength changes and carbon-sequestration capacity in biochar-cement composites. Additionally, long-term durability studies are limited, so the longevity of biochar-cement composites, especially in harsh conditions, remains poorly understood.

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⁶ Like pyrolysis, torrefaction involves heating materials in an oxygen-free environment. Torrefaction is typically carried out at lower temperatures (approximately 200-300°C) than pyrolysis

As a gaseous emission adsorbent, biochar shows great promise for mitigating contaminants from oil and gas wells. Sorption of CO₂, H₂S, CH₄, and VOCs have been demonstrated for various feedstocks and pyrolysis conditions. However, the vast majority of sorption experiments are conducted in highly controlled laboratory studies, leading to uncertainties in the application of biochar for gaseous emission adsorption on a field scale.

The stable carbon content in biochar makes it an asset in global climate change mitigation efforts. It is evident that optimizing biochar production techniques and expanding biochar applications can maximize its environmental benefits. Moreover, there is a need for further research on pyrolysis parameters, with a specific focus on biochar as the primary product. This emphasis on research will help enhance our understanding and utilization of biochar in addressing environmental challenges. In particular, the use of biochar as a cement additive is highly specific to each application, and the specific biochar used must be thoroughly tested in the cement. The variability in biochar also necessitates further research into its use as a sorbent, as the feedstock and pyrolysis temperature have influences on surface functionality which can influence the amount of gases that may be sorbed and the selectivity of the biochar for specific compounds.

Task (3)(a)(II)

Review any applicable federal laws and laws of other states that address the use of biochar in the plugging of oil and gas wells

Plain Language Summary

We reviewed state and federal laws to determine what existing legislation applied regarding the use of biochar or other cement supplements. Biochar and other supplementary materials were not explicitly mentioned in any of the laws or regulations we searched. However, we did find that both the code of Colorado regulations and federal regulations require a variance if any material that is not "normally" used in plugging operations is to be added. Therefore, state and federal approval would be required prior to using biochar in the cement paste.

Methodology

To determine the applicability of any federal or state laws related to the use of biochar in plugging oil and gas wells, we performed keyword searches for biochar in the Colorado Revised Statutes, Code of Colorado Regulations, United States Code, and Code of Federal Regulations. Finding nothing related to biochar from a keyword search, we analyzed the requirements pertaining to well plugging in all four sources from the following regulations and statutes:

- Colo. Rev. Stat. § 34-60-106(1)(c) Mineral Resources [114]
- Colo. Rev. Stat. § 34-61-104 Oil and gas entering coal seams [114]
- Colorado O&G Regulations Section 2 CCR 404-1-434 Abandonment [115]
- Colorado O&G Regulations Section 2 CCR 404-1-408(f) General Drilling Rules [115]
- 40 CFR 144.28(c) Requirements for Class I, II, and III wells authorized by rule [116]
- 40 CFR 146.10 Plugging and abandoning Class I, II, III, IV, and V wells [117]
- 40 CFR 147.305(d)(3) and 40 CFR 147.305(d)(4) Requirements for all wells [118]
- 43 CFR 3172.12 Drilling abandonment [119]
- 42 USC 15907 Orphaned well site plugging, remediation, and restoration [120]
- 42 USC 7436 Methane emissions and waste reduction incentive program for petroleum and natural gas systems [121]
- 42 USC 13368 Ownership of coalbed methane [122]

Regulations for O&G well plugging

The most applicable parameters found at the state level originate from requirements in the Code of Colorado Regulations 2 CCR 404-1-434 [115], which pertains specifically to the abandonment of oil wells. This regulation requires that all wellbores have "water, mud, or other approved Fluid between all plugs." Additionally, "an Operator will not place substances of any nature or description other than that normally used in plugging operations in any Well at any time during plugging operations." Pertaining to the use of biochar in cement specifically, the regulation states that all "cement will conform to the requirements in Rule 408.f." The referenced rule 408.f states that "the Operator will use a cement slurry that isolates all Groundwater, hydrocarbon, corrosive, Potential Flow, or hydrogen sulfide zones." 2 CCR 404-1-502 establishes the requirement for any variances in procedure to be filed with the commission and the approval criteria for such variances [115]. Title 40 of the Code of Federal Regulations, which pertains to

environmental protection, contains similar requirements to the CCR: 40 CFR 146.10 requires that abandoned wells "be plugged with cement in a manner which will not allow the movement of fluids either into or between underground sources of drinking water" but allows for alternative materials if "the Director is satisfied that such materials will prevent movement of fluids into or between underground sources of drinking water" [117]. The requirements for well plugging on federal land are similar, as laid out in 43 CFR 3172.12, and these requirements also allow variances if approved by an authorized officer per 43 CFR 3172.13 [119]. Nothing explicitly pertaining to the use of biochar in plugging operations was found in either the United States Code or the Colorado Revised Statutes. Finally, a keyword search for biochar was performed in the National Council of State Legislatures and nothing pertaining to the use of biochar in oil and gas production/plugging was found in the statutes of any other state.

Biochar and other supplementary cementitious materials

A supplementary keyword search for "supplementary cementitious materials" (SCMs), including "fly ash" yielded no explicit mention of either phrase in either the Colorado or Federal regulations. However, the Bureau of Land Management (BLM) requires that any cement additives must be reported in the drilling plan. Colorado regulations additionally state that "the Operator will prepare cement slurry to: the designed density; minimize free fluid content, to the extent practicable; ensure cement slurry free water separation will not exceed 3 milliliters free water per 250 milliliters of cement; and ensure the cement mix water chemistry is appropriate for the cement slurry design." and that the cement mixture must be tested either every six months or when there is a change in operating conditions, cement type, or cement vendor.

Summary and Recommendations

In the context of oil and gas production, biochar is likely not considered a substance normally used in plugging operations and would therefore be prohibited under this rule. The use of biochar as a cement additive in plugging operations would therefore require either special approval by the commission or a change in the rules. 2 CCR 404-1-502 establishes the requirement for any variances in procedure to be filed with the commission and the approval criteria for such variances [115]. Additionally, the use of biochar as a filler material between cement plugs is not explicitly addressed and is not allowed under existing legislation. As such, approval from and/or a hearing before the commission would likely be required to approve a pilot project involving the use of biochar in any form in oil and gas well plugging.

Task (3)(a)(III)

Conduct desk research related to biochar, including geomechanical modeling and calculations to limit variables

Plain Language Summary

Biochar is a highly variable product, which makes it difficult to model the chemical and physical effects of incorporating biochar into cement, as the results often include high uncertainties. We reviewed geomechanical models related to how cement cures in oil and gas wells and how cement cures when biochar is added. The most commonly used model was the pore partitioning model for predicting cement strength, although it tended to underestimate the compressive strength of the cured mixture. In response to concerns about elevated temperatures and pressures in oil and gas wells, we reviewed a model that relates the effects of varying well temperature on cement curing and identified that higher temperatures could cause faster cement curing. However, this model did not incorporate biochar or other supplementary cementitious materials, so questions remain on how biochar would affect the change in curing rate. After evaluating the literature related to the topic of modeling biochar-cement composites in oil and gas wells, we determined that the uncertainty associated with the biochar itself was too high to confidently predict the behavior of these mixtures and used our literature findings to inform experimental testing, described in Task (3)(a)(IV).

Methodology

To address this task, several existing models and meta-analyses were researched to guide the variables to be tested in the experimental portion (Task IV). We explored models related to cement curing in oil and gas wells and with the addition of biochar. The most relevant models for the application of biochar-cement composites in oil and gas well plugging are presented below, although no models were found that addressed both topics in parallel.

Results and discussion

Several models have been explored to elucidate the chemical reactions and physical interactions responsible for the differences in cement performance after biochar additions in laboratory experiments. Of the models we researched, the pore partitioning model emerged as an important estimator of gel and capillary pore volumes of paste mixtures [123-125]. From the pore partitioning model, performance can be predicted based on porosity, compressive strength, formation factor⁷, and deicing salt damage susceptibility. However, Bharadwaj et al. observed that computational models often fail to consider variability in supplementary cementitious mixtures, leading to uncertainties in the specific chemistries and reactivities of the paste [126]. To address this issue, the authors investigated calcium hydroxide (Ca(OH)₂) formation, as Ca(OH)₂ provides a pH buffer in concrete, which can in turn influence steel corrosion [127], alkali-silica reactions [128, 129] and carbonation [130]. Two fly ashes with differing reactivity were evaluated, and the authors found that as the water-to-binder ratio increased (used as a surrogate for total porosity [131]), the non-evaporable water content also increased from the reaction of fly ash in the

⁷ Ratio of concrete resistivity to its pore solution resistivity

system. For both fly ashes, as the water-to-binder ratio increased, the mass of calcium hydroxide (CH) in the paste increased due to pozzolanic reactions⁸ with ash. Overall, the amount of CH consumed was not enough to cause pore refinement in the system at low replacement levels. However, the authors found that the pore partitioning model underpredicted the amount of CH in the system, especially at higher replacement levels, leading to inaccuracies in cement strength predictions [126] which underestimate the compressive strength of the cured mixture.

A complementary meta-analysis indicates that supplementary cementitious materials can react with water and/or cement hydration products to refine concrete microstructures and potentially improve concrete durability. Durability is often incorporated into sustainability metrics since an increased longevity extends cement lifetime. However, 28-day compressive strength tests yielded no clear trends, underscoring the need for laboratory tests for specific applications [132]. A particular concern for cement longevity is the formation of calcium oxyhydroxides (CaOXY) from calcium in deicing salts, which increases as salt concentration increases. CaOXY formation is problematic as its volume is 303% larger than the volume of Ca(OH)2, which can result in damage to the paste [133, 134]. To better predict cement performance under conditions with high Ca inputs, Ghantous et al. developed a thermodynamic model to determine the volume of hydration products in various mixtures and estimate overall mass fractions. Over multiple temperature cycles, CaOXY formation led to additional void space, which could cause overall decreases in cement strength [135]. While CaOXY formation is expected to be an issue in commercial and residential areas due to road salting, it likely will not have large influences on oil and gas applications as increased downhole temperatures will eliminate freeze-thaw cycles in the space where cement is in contact with salt-heavy geological formation water.

Another issue associated with biochar-cement mixtures in oil and gas applications is associated with increased temperature and pressure compared to ambient conditions. Specifically, as the temperature profile within the well is important for well integrity and flow assurance [136], with concerns for annular pressure [137, 138]. Wang et al. developed a model related to cement hydration kinetics which coupled temperature and pressure, and found that overall, a higher temperature would result in faster hydration and cement curing [139]. However, analysis of the model was primarily focused on heat evolution during the cement curing process, rather than external heat. While the model was able to indicate that high temperatures and pressures can accelerate the cement hydration reaction, it did not indicate whether this change would positively or negatively impact cement performance in the wellbores.

Summary and Recommendations

Our literature review (Task I) revealed that biochar is highly variable, as the physical and chemical characteristics of biochar are determined by both starting material (feedstock) and production treatment. Task III underscored the uncertainties associated with modeling, as the variability in starting material (specifically, biochar variability) cannot be sufficiently addressed at this point in time. Additionally, to our knowledge, there are no existing models which address both biochar behavior in cement *and* the application of such mixtures for oil and gas well plugging. However, the models examined here are helpful for creating hypotheses to guide the experimental portion of this report (Task IV). Per our conversation with Representative

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⁸ Chemical reaction that occurs in Portland cement upon the addition of siliceous and aluminous materials

McCormick on April 3rd, 2024, we determined that modeling experiments would likely not supply sufficient certainty towards the behavior of the biochar-cement mixtures, and instead agreed that a rigorous laboratory approach would be more appropriate at this stage. The results of the experimental section can be found in Task IV.

Task (3)(a)(IV)

Conduct laboratory research, including research to characterize:

- (A) The mechanical strength, permeability, pore structure, and gas absorption of biochar
- (B) The geochemical reaction of biochar with water from an underground formation
- (C) The chemical reaction of biochar with cement used in the plugging of oil and gas wells

Plain Language Summary

Because of the naturally high variability in biochar, we performed strength tests on the specific biochar and cement that is intended to be used in plug and abandonment operations in Colorado. We used biochar made from woody biomass and mixed it in various amounts with Portland cement. We determined the best biochar to use from six different samples based on the elements present in the sample and the particle size. After that, we investigated changes in flow rate and compressive strength with different percentages of biochar added and found that up to 3% biochar addition by weight yielded positive results. Moving forward, we tested controls, 1%, and 3% biochar additions to evaluate how chloride, sulfate, and produced water (geological formation water) would influence strength and found that chloride and sulfate ions caused slight decreases in cement strength over a 28-day time period, but that produced water did not negatively affect the biochar-cement mixtures. Due to the conflicting results, we recommend extending the tests beyond 28 days and repeating the tests with more replicates. Our initial attempts at testing changes in cement strength at higher temperatures were inconclusive, and we recommend repeating the tests using another method described below. Overall, our results show promise for using up to 3% biochar addition in the cement mixture, but further testing is required to build confidence in the results.

Methods

Biochar Characterization

Biochar samples were primarily composed of woody feedstock (75% of starting material or higher) and obtained from Biochar Now, LLC, Charm Industrial, and Biochar Solutions Inc. Biochar Solutions provided four separate biochar samples, differentiated by particle size, for a total of six biochar samples. All six samples are described in **Table 2**.

Table 2. Summary of physical characteristics of the six biochars tested. The particle size of the BC3 sample was unable to be determined due to excessive contamination by inorganic constituents (**Figure B1C**). BC3 and BC1 (**Figure B1A**) samples were excluded from any further testing due to higher proportions of inorganic compounds.

Sample	Average Particle Size (um)	рН
BC1	337.508 +/- 155.75	9.93
BC2	15990 +/- 5119	8.39
BC3	Unable to measure	12.24
BC4	5680 +/- 3961	9.89
BC5	3261 +/-2049	10.34
BC6	38.26 +/- 37.65	11.03

Biochar pH: 1.5g of biochar (n = 6) was added to 30mL DI H_2O and shaken for 30 minutes. Each sample was allowed to equilibrate for another 30 minutes, and the pH was measured and recorded using Orin Star A215 Benchtop pH Meter (ThermoScientific). A second pH was recorded after 24h of equilibration [140].

Biochar particle size: To further investigate biochar physical characteristics, scanning electron microscopy (SEM) was performed. A stainless-steel base topped with carbon tape was inverted onto each biochar without applied pressure. Excess biochar was removed with compressed air applied to the tape with biochar. Each sample was then coated with 5nm gold using an EMS Quorum Q150T ES Plus coater and imaged with SEM (JEOL IT700HR) at a magnification of 200uM, an accelerating voltage of 15kV, and a working distance of 11.2mm. Images were then analyzed in Image J (**Figure B1**). 60 particles were measured along the longest edge of the particle in each sample to calculate an average size per sample [96]. Dynamic light scattering was initially used to size the particles, but it was found that the biochar particles did not stay in suspension long enough to be accurately measured, and each sample was inaccurately reported to be much smaller than their actual size. For this reason, sizing using SEM was carried out instead. Additionally, qualitative energy dispersive X-ray spectroscopy was completed on each sample at the same time as SEM to determine purity.

Biochar water holding capacity: Water uptake was measured using a standard saturated paste percent moisture test. Briefly, water was added to approximately 10g dry biochar until a saturated paste was formed. Any standing water was compensated with additional biochar, and the saturated paste mass was recorded. Percent moisture was then calculated with **Equation 1** [96]. Only sample BC6 (38 nm) was quantified, as this was the only sample able to form a true paste. %moisture = (saturated paste mass-dry mass)/saturated paste mass

Biochar-cement composites

Cement mixing protocol: Class G cement was donated by A Plus Wells (Greely, CO), and a polycarboxylate (PCE) superplasticizer (item #97190) was donated by Fritz-Pak Corporation (Mesquite, TX). All mixes were mixed using industrial supply water. Ratios of water, cement, biochar, and plasticizer used in each test can be found in Table 3. Eight 2"x 4" cylinders were poured for each test using Forney PVC cement molds (LA-0211-24) with caps. Biochar and dry cement were mixed for 1 minute dry before adding water. After water was added and mixture was completely wet, superplasticizer was added during mixing. Combined materials were mixed at high speed for 5 minutes before pouring into molds. Each mold was tamped 30 times after filling halfway, then 30 more times after filling completely. The molds were then capped and left in a heat and humidity-controlled room until demolding [141]. Demolding was accomplished by puncturing the bottom of the mold with a nail, then adding compressed air until the cement cylinder was released.

Compressive strength: Compressive strength was measured using a Forney F-1500KN-VFD Automatic Compression Test Machine, which records stress applied to a sample every ~0.3 seconds until failure (pressure loss >100 PSI in one 0.3 second interval with no recovered

pressure), or the sample is compressed enough that the machine no longer registers its presence. Compressive strength was measured every 1, 4, 7, and 28 days after each test started. It should be noted that only stress was measured and no strain data was collected; therefore, Young's Modulus could not be calculated.

Effect of Particle Size: To determine the optimal biochar particle size for the biochar-cement composites, a 3% mix with BC6, BC4, BC5, or BC2 samples were created following the cement mixing protocol described above. Samples were left unground and dry prior to mixing. Compressive strength testing indicated that sample BC6 yielded the best results, so all remaining testing was performed only with biochar BC6. BC3 and BC1 samples were excluded due to impurity.

Cement slurry viscosity: Viscosity was measured using the Zahn cup method (ASTM D 4212, D 816, D 1084). After the cement was fully mixed, the no. 3 Zahn cup (3.86mm) was fully submerged in the mixture and allowed to drain. The time from the start of draining to the breakup in the fluid stream was recorded and kinematic viscosity was calculated in centistokes [142]. The correct mass of superplasticizer needed to compensate biochar addition was elucidated by comparing the viscosity the control mix (no biochar), and PCE was added to biochar mixtures until similar viscosities were achieved [141].

Chloride and sulfate sorption: Control, 1%, and 3% mixtures were tested to determine cement resilience to common anions. Cylinders of each cement mixture were demolded after 1 day of curing, and each cylinder was placed in its own plastic container with either 0.7M NaCl or 0.012M Na₂SO₄ (450 mL). Two cylinders of each mixture were tested for compressive strength after soaking for 1, 4, 7, or 28 days [99]. After the cylinders were removed, the concentrations of chloride and sulfate in the remaining solution were determined using ion chromatography (Dionex ICS-2100 Ion Chromatography System) to elucidate ion sorption to the cement mixtures [143].

Produced water vulnerability: To investigate the vulnerability of cement to underground formation water, cement mixtures were exposed to produced water collected from the Niobrara formation of the Denver-Julesburg basin in December 2020 [144]. The produced water was stored in closed containers at 4 °C prior to use. Compressive strength testing indicated that the 3% biochar mixture performed better than or similarly to the control, (depending on amount of time curing), so the 1% mixture was omitted from further testing. Cylinders of control and 3% biochar mixture were demolded after 1 day of curing, then immediately submerged in produced water. Produced water (PW) was placed in a 2-chambered glass tank (9 L each chamber), and control or 3% cylinders were submerged in either chamber. Two replicates of each cement mixture were tested for compressive strength after soaking for 1, 4, 7, or 28 days. Major organic chemical constituents of the produced water can be found in **Table B1**.

Gas sorption: Nitrogen sorption capacity of a fully cured (28 days) cement was tested with BET analysis (Micrometrics ASAP 2020 Surface Area and Porosity Analyzer) [99]. Fully cured (28 days)

cement was crushed to pea-sized pieces before testing and degassed for 24 hours prior to analysis.

Effect of heat on curing: Cement cylinders were demolded after 1 day of curing and placed in a glass tray containing $^{\sim}1$ L DI H₂O and sealed with a flat plane of glass. The trays were then placed in an oven at 90 $^{\circ}$ C, and water trays were refilled daily. After 1, 4, 7, or 28 days, cylinders were removed, and compressive strength was measured.

Table 3: Cement to biochar ratios for each mixture. Mass amounts are for a single batch of mixing (8 cylinders). PCE is the polycarboxylate ether plasticizer used in all samples. Stars indicate excess plasticizer was used to attain the lowest possible viscosity (figure B4).

Biochar- Cement Mixture	Cement (g)	Water (mL)	Biochar (g)	PCE (g)	Mass Ratio (cement:water:biochar:PCE)
Control	2380	1047.2	0	0	1:0.44:0:0
1%	2380	1047.2	23.8	0	1:0.44:0.01:0
3%	2380	1047.2	71.4	8	1:0.44:0.03:0.003
5%	2380	1047.2	119	32*	1:0.44:0.05:0.0134
10%	2380	1047.2	238	46.6*	1:0.44

Results

Biochar pH

The pH values of the 6 tested biochar samples are summarized in **Figure B2** and **Table 1**. All samples were alkaline, ranging from 8.46 (BC2) to 12.26 (BC3), which is in line with previous studies [140]. Sample BC6 had a pH of 11.03 after equilibration; this sample is used in all subsequent tests except when noted. Cement has been reported to have higher short-term compressive strength in an alkaline setting [145], potentially due to accelerated setting due to inhibition of Ca²⁺ release from the gypsum component of cement, leading to accelerated hydration. However, in the long term, alkaline cement tends to be more porous, and may be more vulnerable to cracking than neutral cement [146]. Since biochar tends to be slightly alkaline, it is important to consider this when assessing the compressive strength of cement containing biochar.

Biochar size

Particle size varied greatly within each sample, although particle shape was consistent between samples. Since biochar forms in a somewhat honeycomb pattern, broken pieces tend to be rectangular while larger pieces are squarer (**Figure B1**). Larger particles were far more porous than more finely ground particles. Average particle sizes of the biochar samples reported in **Figure B3** and **Table 1**. Two of the samples showed significant aluminosilicate contamination (confirmed by EDS, **Figure B1A and B1C**) – BC1 and BC3 – and were excluded from further testing. It has been previously reported that particles smaller than 200um performed best in cement mixtures [94, 96], which would include only sample BC6 of the six biochars tested. Indeed, in all cases except

with sample BC6, with an average size of 38.26 +/- 37.65 um, the biochar separated from the mixture cement entirely, forming a biochar layer on top of the curing cement (Figure B6). Because only sample BC6 was able to blend homogeneously with the cement, all remaining tests used only sample BC6.

Biochar/cement surface area and porosity

It is well-established that increasing the porosity of a cement will decrease its compressive strength [147], so it is important to investigate any changes to porosity when adding a highly porous material such as biochar. Porosity of the samples were measured using BET once the cement had fully cured (>28 days since pouring). To keep the curing time consistent between samples, only the samples cured underwater and the 3% mix cured dry were tested. The samples were crushed to pea-sized pieces before analysis. The BET results for surface area and porosity of the samples are summarized in **Table 4**. Although biochar is known to be highly porous, previous studies have shown that the addition of biochar to a cement decreases the porosity of the cement once it is cured, because water absorbed by the biochar in the initial curing stages of the cement is allowed to seep out over time, aiding in internal curing and decreasing pores in the cement [96]. Our results show that while pore volume stays very consistent between samples, pore size can be reduced if the sample is cured underwater. This is the same concept that sometimes leads to smaller pores in biochar-cement composites, but our samples may not have enough biochar to see that noticeable of an effect. Gas sorption of the samples was tested using nitrogen gas. At the highest pressure (500mmHg), 79 cm³/g STP of N₂ was sorbed by the 3% sample cured underwater, compared to 63 cm³/g STP in the underwater control sample (Figure B7). This suggests higher gas sorption potential of the biochar cement over the cement alone, which is in line with previous studies [96]. Future studies must be conducted to determine the actual amount of various gases which could be sorbed by each biochar-cement composite.

Table 4. Summary of surface area, pore volume, and pore size data collected by BET of fully cured biochar-cement mixtures. "H2O" signifies that the sample was cured underwater

Sample	BET Surface Area (M ² /g)	Total Pore Volume (cm³/g)	Average Pore Size (Å)	N ₂ Sorbed (cm ³ /g STP)
3% biochar- cement	33.4863	0.108994	130.1953	70
3% biochar- cement (H₂O)	51.5085	0.1185	90.6819	79
1% biochar- cement (H₂O)	29.3053	0.0792	106.2964	52
Control cement (H₂O)	39.9879	0.097	94.6526	63

Biochar water holding capacity

When adding a highly absorbent material to cement, such as biochar, it is important to consider any water absorbed by the additive, which removes the water from the curing process. The percent moisture of sample BC6 was 75.43% +/- 0.0023%, indicating it holds up to 75.43% of its own mass in water. In concrete samples with biochar, this means 18-90 mL of water is removed from the curing cement, making a water reducing superplasticizer (such as PCE) necessary.

Cement slurry viscosity

Superplasticizers are commonly used in all types of cement to improve workability. Different plasticizers can affect varying aspects of cement curing (e.g., delayed setting, cured color), but plasticizers consistently lower slurry viscosity. In this case, low viscosity is the most important feature the slurries must display, so a plasticizer that has been shown to most efficiently lower viscosity (PCE) was chosen [148]. The 10% mixture was excluded before compression testing due to workability – even at its lowest possible viscosity, the slurry did not flow. Low cement viscosity is important to prevent clogging by the machines used to plug wells, and the 10% mixture with excess plasticizer (lowest viscosity) was a non-Newtonian fluid that did not flow without pressure. The 5% mixture also performed poorly and was excluded from further investigation. However, we were able to achieve reasonable viscosity from 3% biochar and below (Table 5), as determined by the range in which the viscosities fell. Although the difference between the viscosities may seem dramatic, they are all still considered to be low viscosity fluids: At the lowest viscosity, the control sample has a consistency similar to maple syrup, while the highest viscosity sample that showed any promise (3%) had a consistency similar to apple sauce. All samples fall in the range of viscosities seen in motor oils and are significantly less viscous than materials such as honey (2000 centipoise; cP) or caulk (5,000,000 cP). Since viscosity is an important variable for industrial application and increases with increasing biochar, further consultations with industry partners are recommended to ensure the viscosity remains within a workable range for P&A operations.

Table 5. Slurry viscosities of all tested biochar-cement mixtures

Mixture	Control	1%	3%	5%	10%
Kinematic	72.31	95.82	286.65	336.26	Infinite/does not flow
Viscosity	+/- 0.48	+/- 0.42	+/- 0.33	+/- 0.67	
(cSts)					
Dynamic	135.69	181.84	542.44	632.16	
Viscosity	+/- 2.82	+/- 3.16	+/- 2.06	+/- 2.67	
(cP)					
Comparison	Maple syrup	Tomato	Apple sauce	Castor oil	Silly Putty
		juice			

Biochar as a cement additive

Average compressive strength of different weight % biochar-concrete mixtures can be found in **Figure 5**. While other samples showed a clear point of failure, the 5% samples showed a gradual failure over time, making determination of stress at break impossible. Because of this,

the point at which plastic deformation (referred to as "stress at break") begins (**Figure B5**) is reported instead. Due to the lower recorded compressive strength, the 5% sample was excluded from further testing. Although the 3% and 1% samples initially showed improved compressive strength (through the first seven days of testing), by 28 days, the control, 1%, and 3% samples all displayed similar compressive strength. Initial improvement in strength could be due to the alkalinity of the biochar samples as discussed above, or could be the result of improved water retention through biochar addition, allowing for superior internal curing [96].

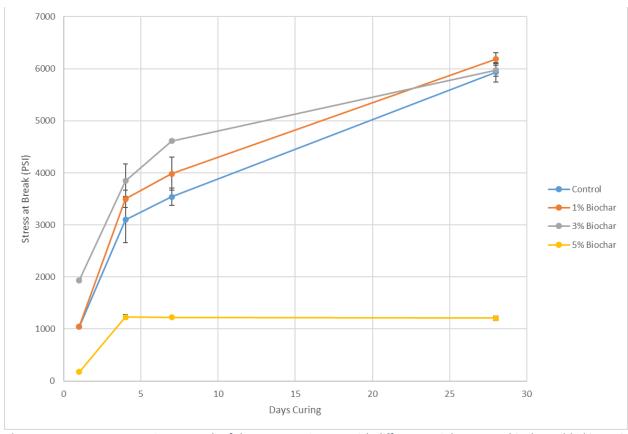


Figure 5: Average compressive strength of the cement mixtures with different weight percent biochar added in. n=2 to n=4 cylinders tested at each time point. 5% biochar mixture stress at break is recorded as the point of plastic failure (**figure B5**), as true stress at break in this sample could not be determined.

Chloride and Sulfate Sorption

Attack by anions such as sulfate and chloride is a major concern for the longevity of concrete in the environment, especially as geological formation water is expected to contain high concentrations of chloride. Sulfate ions can react with calcium hydroxide and calcium aluminate hydrate present in the curing cement and cause the material to soften and expand, leading to cracking [149]. While it seems the primary concern with chloride attack is steel reinforcement corrosion, it is still widely reported that chloride can weaken the concrete as well [150], which could be caused by chloride expansion of the pores in curing cement, allowing more water to enter. We observed this weakening in our biochar cements as well. Soaking curing cement in a solution of chloride or sulfate resulted in slight decreases in cement strength compared to a water

control in all mixtures (**Figure 6**). The effect was much less pronounced in the sulfate solution than the chloride solution, but this may be because the chloride solution was far more concentrated, reflecting values commonly seen observed in produced water. Although all samples were affected, we observed slightly higher decreases in the 1% and 3% mixtures compared to the control, possibly indicating biochar addition makes a mixture more vulnerable to anion attack. However, further research is needed to fully elucidate potential strength changes to cement mixtures exposed to high anion concentrations.

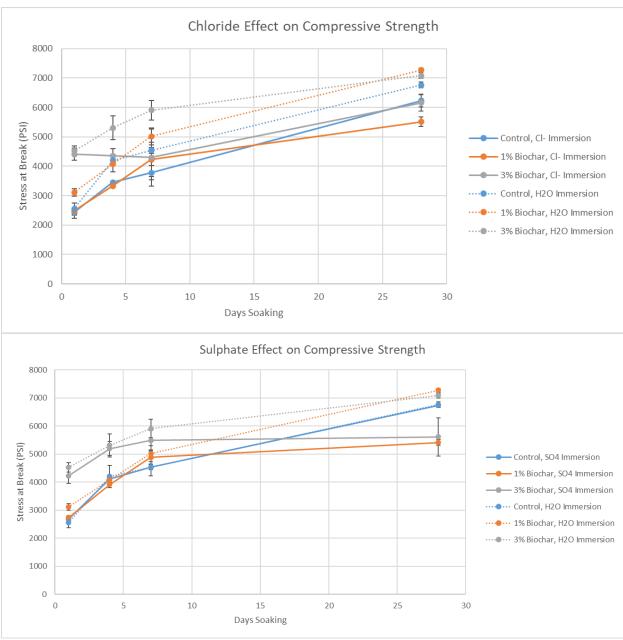
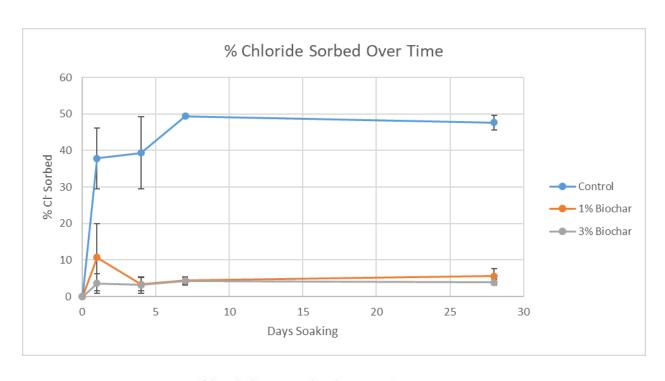


Figure 6. Stress at break in cements soaked in a 0.75M chloride solution (top) or a 0.01M sulfate solution (bottom). Cement was demolded after 1 day and submerged in solution for 1, 4, 7 or 28 days, then compressive strength tested. Dotted lines represent a parallel test in which a separate set of cylinders were soaked in DI water as a control. n=2 to n=4 cylinders tested at each time point.

Biochar addition also dramatically changes the sorption behavior of the anions to the cement. In the chloride test (**Figure 7**), the control sample had high initial sorption rates, which then equilibrated over time. The 3% and 1% mixtures displayed the same trend, but on a much smaller scale. While the control sample began to equilibrate at 4 days of soaking and sorbed 51.2% of the chloride in solution, the 1% and 3% samples equilibrated after 1 day and only sorbed 11.6% and 4% of the chloride respectively. Additionally, the control sample seemed to continue to equilibrate after 28 days, while biochar samples slowly sorbed more chloride over time and did not appear to reach their sorption capacity in the 28-day testing period., supporting the theory that biochar decreases the resistance of the cement to chloride attack. Therefore, we recommend extending the tests beyond the 28-day period.

Of the three samples, the control was the least affected by sulfate attack, but also had the highest sulfate sorption (**Figure 7**). Unlike chloride, the control samples in the sulfate solution did not seem to reach max sorption within 28 days. The initial results suggest that biochar slows the sorption of sulfate but may make the cement more vulnerable to any sulfate sorbed. To determine any potential trends, this test should be repeated at a higher concentration of sulfate and continue for a longer time.

Produced water is a complex and highly heterogeneous material, containing other anions such as nitrates, cations such as Mg²⁺, Fe²⁺ and Fe³⁺, Al³⁺, and Ca²⁺, and organic compounds such as hydrocarbons (**Table B1**). When submerging samples in produced water, the 3% sample performed best, but by 28 days, the 3% and control samples seemed to converge at the same compressive strengths (**Figure 8**). Interestingly, although chloride and sulfate concentrations in the produced water were similar to the concentrations used in the chloride and sulfate tests alone, the data from the produced water tests diverged from the results from the single-ion tests. This suggests that although biochar weakens the cement with chloride and sulfate, there may be other chemical conditions that favor the development of cement strength amended with biochar in the produced water. The slightly negative charge on biochar particles may be able to facilitate weak cation sorption, allowing easier uptake of Ca²⁺ in the 3% sample compared to the control. Gradual desorption of Ca²⁺ in the curing cement may add integrity to the mixture, offering a possible explanation for the apparent increased strength in the 3% sample[151]. This result warrants further investigation, as neither cation sorption of biochar nor of the biochar/cement composites were investigated in this study.



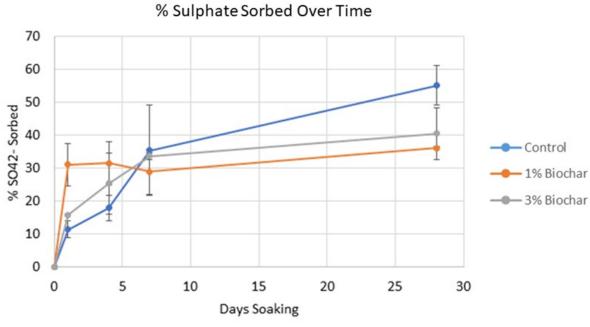


Figure 7. Sorption of chloride (top) and sulfate (bottom) by 1%, 3%, and control mixes. The concentration of chloride of sulfate in the initial solution (days soaking=0) was compared to solutions taken once cement cylinders were removed after soaking for 1, 4, 7, or 28 days. Containers were airtight, and any changes to ion concentration were assumed to be from sorption by the cement. n=2 to n=4 cylinders tested at each time point

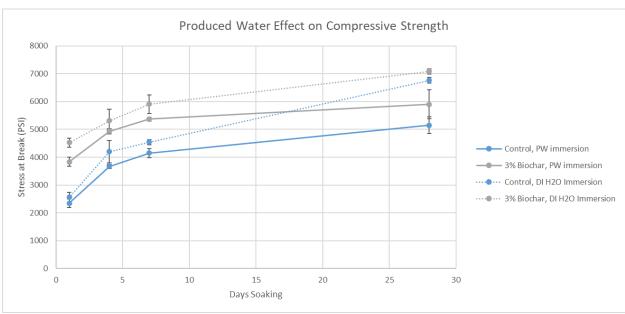


Figure 8. Compressive strength of biochar cements immersed in produced water (PW) or DI water for 1, 47, or 28 days. Each data point represents an average of 2 cylinders broken. Information on PW composition can be found in **Table B1** [144].

Summary and Recommendations

Biochar-cement composites were tested at 1-10 weight % biochar addition, with the results summarized in **Table 6**. The mixture with 3% biochar was determined to be the highest amount of biochar that could be added without increasing viscosity to a point where the workability of the mixture was not compromised. We observed slight decreases in 28-day compressive strength of biochar-cement composites exposed to sulfate and chloride ions compared to unamended controls, although exposure to produced water had the opposite effect. Overall, the preliminary data is promising for the for the application of biochar in P&A operations, although further testing is required.

A primary concern for cement mixtures in P&A operations is performance under high temperatures, as oil wells may have high downhole temperatures [152]. While a full 28-day test at a constant 90°C was completed, the samples were unable to remain sufficiently hydrated throughout testing, leading to several instances in which the samples dried out. Large variabilities in cement strength and overall poor testing conditions created large inconsistencies in the data, leading to inconclusive test results. Dehydrated cements are weaker than hydrated cements, and due to the high humidity in oil wells, this test does not accurately represent the true strengths of the mixes as they would be subjected to high heat in an oil well. We are currently retesting the heat tolerance of all the cement/biochar mixtures using a different experimental setup to ensure no samples can dry out, but these results are incomplete prior to the completion of this report. Additionally, polycarboxylate plasticizers are not typically used in well plugging operations; thus, future studies must incorporate the appropriate plasticizer.

Table 6. Summary of results of the variables explored for biochar addition to cement. The relevant task from the house bill is identified, and preliminary conclusions and recommendations for future studies are presented.

Test	HB Task	Preliminary	Recommendation
		Conclusions	
Weight Percent	Mechanical strength "Chemical reaction of biochar with cement"	Biochar can be added up to 3% by mass without compromising strength at 28 days. Only 1% can be added without compromising strength if a higher viscosity cannot be tolerated.	Investigate viscosity limits of industrial use. Extend trial past 28 days
Sulfate Resistance	Permeability	Biochar-cement	Extend trial past 28
Chloride Resistance		samples do not perform as well as control when immersed in anion solution. However, the presence of biochar slows the sorption of chloride or sulfate to the curing cement.	days
Produced Water Resistance	Biochar with water from an underground formation	3% mixture shows increased strength at 28 days compared to	Investigate possible mechanisms, including cation
		control.	sorption. Extend trial past 28 days.
Heat Resistance	Geomechanical modelling	3% sample more vulnerable to dehydration than control	Retest ongoing

Task (3)(a)(V)

Evaluate whether any federal or state programs or private entities could provide funding for the pilot program

Several programs exist that may provide funding for a pilot program related to orphan well plugging. The Bipartisan Infrastructure Law Section 40601(d) provides \$4.7 billion for orphaned well plugging, remediation, and reclamation to eliminate environmental and public safety hazards (CITE). The funding is distributed by the Department of the Interior and is guided by the Orphaned Wells Program Office.

The funding from the Bipartisan Infrastructure Law is divided into three programs:

- The State Orphaned Wells program, receiving \$4.3 billion
- The federal Orphaned Wells program, receiving \$250 million
- The Tribal Orphaned wells program, receiving \$150 million

Under the State Orphaned Wells program, a state may use funding to remediate or reclaim orphaned wells on state and private land. Additional information is available at https://www.doi.gov/state-orphaned-wells-program.

Additional funding to research methane mitigation strategies may be available through the Methane Emissions Reduction Program, under the purview of the Environmental Protection Agency. Specifically, financial assistance may be available for projects related to "reducing methane and other greenhouse gas emissions from petroleum and natural gas systems by improving and deploying equipment to reduce emissions, supporting innovation, and permanently shutting in and plugging wells". For additional information, visit https://www.epa.gov/inflation-reduction-act/financial-and-technical-assistance-methane-emissions-reduction-program.

Finally, several companies have shown interest in the work described in this report and may be able to provide private funding for a pilot program.

Task (3)(a)(VI)

Assess the costs associated with using biochar in the plugging of an oil and gas well

Plain Language Summary

The cost analysis entails a comparison between traditional well plugging methods and those utilizing biochar. An assessment was conducted on a vertical well with a depth of 6800 ft, considering a biochar purchase price of \$209 per tonne without valuing any emissions reductions for CO_2e . A spacer mixture comprising 15% weight biochar is employed to fill the well sections not occupied by cement. The cement slurry for the well plugging operation incorporates 3% biochar by weight. The economic analysis determined that utilizing biochar for well plugging necessitates 4.2 tonnes of biochar and incurs a cost of \$47,199, while the absence of biochar results in a cost of \$46,2169. The inclusion of biochar raises the overall cost by slightly over 2%. The spacer mixture retains 92% of the biochar, with the remaining 8% being utilized in the cement slurry. Owing to the lack of available research on the use of biochar as a spacer fluid additive, further testing is warranted to validate its properties and ensure compliance with well plugging requirements.

Methodology

The successful implementation of a biochar production system in well plugging depends on the economic feasibility of the entire process. To determine economic feasibility, a detailed economic analysis to assess cost-effectiveness is required. Wells that are no longer economically viable or no longer in use must be plugged to prevent the migration of gas or fluids, which could lead to environmental contamination and safety hazards [153]. The costs associated with well plugging can vary widely, ranging from a few thousand dollars to several hundred thousand dollars per well, influenced by factors such as well depth, geological conditions, and the duration the well has been idle [154].

An economic analysis was conducted to calculate the operating costs involved in the well plugging process for a vertical well with a depth of 6800 feet, with the cost of biochar estimated at \$209 per tonne based on values reported by industry sources¹⁰ [155-161]. The analysis included various cost components such as labor, plugging materials, equipment usage, and rental items. Standard equipment required for well plugging includes a bulk truck, a triplex truck, and a workover rig [153]. The materials used in the well plugging process typically include cement, water, and bentonite, used in either the cement slurry or the well plugging spacer fluid [162]. The cement slurry used in the analysis consisted of a mixture of Portland class G cement, water, and bentonite.

Site preparation for well plugging includes wireline operations to assess the integrity of the existing well casing [163]. In areas where the well casing is compromised, a squeezing operation is performed to reestablish its integrity before cementing [164]. The wellbore is then plugged to ensure proper isolation between liquid and gas formations and to protect any groundwater zones. Spacer is used to fill the volume of the well not occupied by cement, and this spacer material is a slurry composed of water, bentonite, and biochar [165]. In this analysis, the

⁹ Cost evaluated in 2024 USD

¹⁰ Biochar prices accessed February 2024

spacer mixture includes bentonite at 5% by weight [165], and biochar is assumed to be added at 15% by weight based on communication with well plugging operators. The cement slurry mixture includes Portland cement, water, and biochar at 3% by weight. Once the plugging and abandonment process is complete, operators are required to submit detailed logs to the Colorado Energy & Carbon Management Commission (ECMC) documenting the well abandonment process that contain critical information such as the number of plugs placed, the quantity of materials used, and other relevant parameters [155]. The data from these logs, along with insights from relevant literature and communication with well plugging operators, were used to determine standard operations and cost values for conventional vertical well plugging processes. Additional parameters and assumptions used in the economic analysis are provided in **Appendix C**.

Results and Discussion

The cost analysis of well plugging operations shows a detailed comparison between conventional methods and those incorporating biochar. The total cost for plugging wells using biochar is \$47,199. This amount includes the combined expenses for materials, equipment, labor, and other operational needs specific to the inclusion of biochar in the well plugging process. In comparison, the total cost for plugging wells without using biochar is slightly lower, at \$46,216. This results in an additional \$983 in well plugging costs, with uncertainties ranging from \$287 to \$1,629 in costs. These variations depend on biochar prices, which range from \$58 to \$348, and transportation distances, which range from 40 to 200 miles roundtrip. **Figure 9** includes the standard costs associated with well plugging operations with and without the addition of biochar, covering major materials and processes associated with a typical well plugging operation.

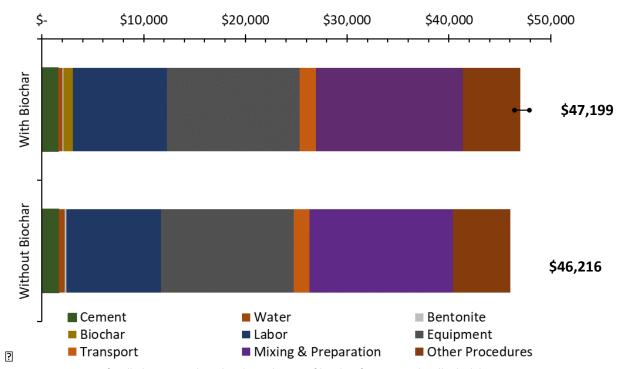


Figure 9: Average costs of well plugging with and without the use of biochar for a vertical well. Black line represents uncertainty with biochar use in well plugging.

In a standard well plugging operation that does not utilize biochar, the primary cost contributors include equipment use, mixing and preparation, and labor. Among the equipment costs, the workover rig represents the most significant expense, accounting for 17% of the total well plugging cost. Within the mixing and preparation process, the bulk material mixing charge is the highest contributor in this category, also at 17% of the total cost, followed by the wireline operation, which contributes 11% to the overall cost. ECMC states that in 2022, the average cost of a well plugged in Colorado is \$52,141, which aligns with the value found in this analysis [166].

The incorporation of biochar into the well plugging process uses 4.2 tonnes of biochar and increases the overall plugging cost by \$983, which represents just over a 2% increase compared to plugging without the use of biochar. The well spacer fluid comprises 92% of the biochar addition. The primary cost contributors of biochar addition include the purchase price, transportation fees, and additional fees in bulk mixing charges. The cost range for U.S. bulk biochar prices is between \$58 and \$348 [156-161] and adjusting for this minimum or maximum would result in a cost adjustment ranging from \$46,556 to \$47,787. Local biochar producers in Colorado charge \$188 per tonne, which would correspond to a well plugging cost of \$47,108.

When using biochar in the spacer at a 15% weight replacement, the average density of the spacer fluid decreases from 62 lb/ft³ to 59 lb/ft³. The density of the spacer composition is important for effective fluid displacement within the well [165]. The bulk density of biochar can vary based on the input biomass and thermochemical conversion method, leading to variability in the spacer density. In this analysis, a bulk density of 0.73 g/cm³ from slow pyrolysis of pine wood biomass was utilized [167]. However, there is limited research available on biochar in well plugging spacers. Despite the slight change in density, further testing is necessary to confirm the compatibility of the biochar, bentonite, and water spacer mixture as a well plugging fluid, given that 92% of the biochar is incorporated in the spacer. Successful integration is crucial for maximizing biochar use and determining its value in emissions reductions.

Summary and Recommendations

Incorporating biochar into well plugging operations results in a 2% cost increase. However, it has the potential to enhance the environmental sustainability of operations and provides an opportunity to earn additional revenue through carbon credits (see Task (3)(a)(VIII) for more details) [168]. This financial incentive could make biochar a more attractive option, encouraging greater adoption of environmentally beneficial practices in the well plugging industry. While the integration of biochar at a 15% weight replacement in the spacer fluid slightly decreases its density, further testing is essential to ensure the compatibility and effectiveness of the biochar, bentonite, and water mixture as a well plugging fluid, thereby maximizing its use and potential for emissions reduction.

Task (3)(a)(VII)

Determine the amount of biochar that is available for use in the state

Plain Language Summary

This analysis utilized Forest Inventory and Analysis (FIA) data, a nationwide inventory managed by the USDA Forest Service, which includes field measurements of tree species, diameter, and height across a network of plots. The FIESTA package in R was employed to assess data from 2010-2019 for non-reserved lands in 40 Colorado counties. By filtering for standing dead trees, the analysis estimated the total salvageable material at 7.14 billion cubic feet. This volume could potentially yield 1,999,490,038 CCF, or 41,333,205,500 tons of biochar.

Methodology

Overview of Forest Inventory Analysis

The core dataset used for this assessment is the Forest Inventory and Analysis (FIA) inventory, a nationwide inventory of US forestlands maintained by the USDA Forest Service. The program is designed to assess the status and trends of forests across all land ownerships and forest types. The network is comprised of permanent, geographically unbiased field plots at a density of approximately one per 6,000 acres [169]. All annual inventories follow a nationally standardized, fixed-area, mapped-plot design. Each plot has four non-overlapping 24 ft. radius circular subplots, which cover about 1/24 acre. For all subplots, substantial forest mensuration data¹¹ are collected, which include conifer and hardwood species. The species identity, diameter, and height of every living and dead tally tree is measured and recorded. The FIA program defines forest land as land that has at least 10 percent canopy cover of live tally tree species of any size, or land formerly having such tree cover, and not currently developed for a non-forest use. The minimum area for classification as forest land is 1 acre. Roadside, streamside, and shelterbelt strips of trees must be at least 120 feet wide to qualify as forest land [170]. Additional details on inventory design and forest land definitions are provided in Bechtold & Patterson [169] and can be found at Colorado State Forest Service's (CSFS) FIA webpage: https://csfs.colostate.edu/forestmanagement/forest-inventory-analysis/.

The FIA program estimates tree volume by combining field measurements with mathematical models. The field crews measure the diameter, height, and species of each tree. Analysts then use these field measurements and species-specific equations to estimate the weight of different tree components, and thereby the total tree volume. This assessment incorporates estimates from FIA's National Scale Volume and Biomass (NSVB) system released in October 2023 to estimate volume. The NSVB approach is only for timber species (trees where diameter is measured at breast height). The update incorporates new data for more scientifically accurate and consistent predictions of tree volume, including new equations for components such as the non-merchantable top. The previous method, called component ratio method (CRM) is applied for woodland species (trees where the diameter is measured at root collar). The component ratio method (CRM) was developed by Heath et al. [171], and until the release of NSVB, was the national approach for biomass and volume estimation used by FIA. CRM applies

 11 Includes dimensional data (e.g., diameter, height, volume), form, age, and increment of trees

equations from destructive sampling studies in which trees are cut down, separated into their component parts, and volume and biomass are calculated [170]. Tree volume estimates can be extrapolated from the plots to larger areas, like a county or state.

This analysis used the most recent 10-year panel of FIA data available in Colorado: 2010-2019. It only considers non-reserved land with the exception of state land (see below), and only standing, live trees.

County, ownership, and forest type

The location grouping chosen for this analysis is Colorado counties. The county level was chosen because 1) it is consistent with the statewide carbon accounting report, 2) it allows for Green-book methodology estimates (see below), and 3) it is consistent with FIA's standard population tables. This study initially assessed all counties in Colorado, which was then refined to 40 counties based on the presence of FIA's forest definition. Many counties within Colorado's Front Range and on the eastern plains were excluded due to lack of forest cover and insufficient FIA plot coverage (i.e., Broomfield, Cheyenne, Crowley, Denver, Kiowa, Kit Carson, Lincoln, Morgan, Phillips, Prowers, Sedgwick, Washington, and Weld counties). Counties with forest cover were excluded if they had a percent standard error equal to or exceeding 25% for gross cubic-foot volume. This included Adams, Alamosa, Arapahoe, Baca, Bent, Elbert, Logan, Otero, Pueblo, and Yuma counties.

The four CSFS areas (Northwest, Northeast, Southwest, and Southeast) were used to clump counties together for visual purposes. The CSFS areas follow Colorado county lines except Park County, which is divided between the SE and SW areas. More than 50% of the geographic area is in the SW area, so it was placed in the SW area.

Next, volume estimates were assessed by land ownership. We used the four FIA ownership groups, which are made up of similar owner classes (**Table 7**). The FIA program further distinguishes land ownership by reserve status. Reserved land is land withdrawn from management for production of wood products through statute or administrative designation. Examples of this include designated Federal wilderness areas, national parks and monuments, and most state parks (FIA Glossary: Standard Terminology, 2022). This assessment only considered land that is non-reserved among each owner class except for State land. In Colorado, only the Bureau of Land Management (BLM) and Departments of Defense/Energy contain non-reserved land in the "other federal entity" ownership group (land owned by the National Park Service, Fish and Wildlife Service, and Other Federal were excluded in this assessment).

Reserved land was included for state land because FIA designates all state land in Colorado as reserved, except for State Forests. The Colorado State Forest in Walden County is categorized as a State Park, which makes it "reserved" although it has a multi-use land management framework which includes management for production of wood products [172]. In addition, there are other state-owned areas in Colorado owned by the Colorado State Land Board, which are not classified as a State Forest, and management for production of wood products does occur. Appendix L of the FIA Database Manual contains further information on reserved status by ownership and land designation [170].

Table 7. Classification of FIA ownership groupings detailing specific owner classes within each group and their respective owner classes as utilized in this assessment, including reserve status distinctions.

FIA Ownership Group	FIA Owner Classes	Owner Classes used in this Assessment	
Forest Service	National Forest; other Forest Service land	National Forest (non-reserved)	
Other federal entity	National Park Service; Bureau of Land Management; Fish and Wildlife Service; Departments of Defense/Energy; Other Federal	Bureau of Land Management (non- reserved) and Departments of Defense/Energy (non-reserved)	
State and local government	State including State public universities; Local (County, Municipality, etc.); Other Non-Federal public	State (reserved and non-reserved); local (reserved); other non-federal public (non-reserved)	
Private and tribal	Undifferentiated private and Native American	Private and Native American (non-reserved)	

The amount of standing volume in the state was further estimated by forest type. We used the FIA Species Group Code (SPGRPCD) to classify forest types. Each tree species in Colorado is assigned a species group. For example, white fir (Abies concolor), subalpine fir (Abies lasiocarpa), and corkbark fir (Abies lasiocarpa var. arizonica) are in the True fir species group. There were 25 tree species and 10 tree species groups used in this assessment. Refer to D1 for individual tree species and corresponding species group codes. The ten species groups in this assessment include: Douglas-fir, ponderosa pine, true fir, spruces, lodgepole pine, pinyon-juniper, other western softwoods, cottonwood and aspen, other western hardwoods, and woodland hardwoods.

The species groupings used in this assessment differ from CSFS's 10 forest cover types. The CSFS forest cover types are based on the dominant overstory vegetation, and the species group codes used in this assessment do not focus on dominant vegetation. An FIA plot can contain multiple species group codes among all layers (overstory, intermediate, understory) offering a more detailed representation of species present for quantifying volume across Colorado's landscapes.

Analysis

All analyses were completed in R and primarily used the FIESTA (Forest Inventory ESTimation and Analysis) package, an open-source research estimation tool for analysts that work with sample-based inventory data from the USFS's FIA program. FIESTA can generate traditional statewide estimates while also accommodating county boundaries, different evaluation time periods, customized stratification schemes, integration of multi-scale remotely sensed data and interaction with other modeling and estimation tools from CRAN's library of packages [173]. We chose FIESTA for this analysis due to its diverse functions that allow for querying FIA data, summarizing and compiling data, and creating estimates with corresponding sampling errors.

Inputs required to generate FIESTA outputs include area of interest, FIA plot data, and auxiliary data. FIA plot data must be downloaded and correspond to the area of interest. Because

our chosen geographic boundaries were counties, we were able to utilize the standard FIA state-level population data, requiring no spatial or auxiliary work. The Colorado SqLite database was downloaded from the FIA DataMart on October 3, 2023. Next, the Green-Book (GB) functions in FIESTA were used for analysis. The Green-Book (GB) method is the standard FIA method for producing nationally consistent forest estimates, associated standard error, and is based on Bechtold and Patterson [169]. The GB method adjusts for nonsampled conditions, supports post-stratification for reducing variance, and reports by estimation unit or a summed combination of estimation units [173]. This allows the estimates to be summed at the state level.

To quantify standing dead material across Colorado's forests we used FIA's VOLTSGRS volume variable. For timber species (trees where the diameter is measured at breast height (DBH)), the VOLTSGRS estimate captures trees ≥ 1.0 DBH and is the total cubic-foot volume of wood in the central stem from ground line to the tree tip. For woodland species (trees where the diameter is measured at root collar (DRC)), the VOLTSGRS estimate captures trees ≥ 1.5 inches DRC and is the total cubic-foot volume of wood and bark from the DRC measurement point(s) to a 1.5-inch top diameter, including branches that are at least 1.5 inches in diameter along the length of the branch [170](**Table 8**).

Table 8. Descriptions and species groupings for the four variables estimated in this assessment. The descriptions differ for timber species (softwoods and hardwoods, measured at DBH) and woodland species, measured at DRC. DBH is the diameter at breast height. DRC is the diameter at root collar [170].

FIA Species Type	Description	Species Grouping
Timber	The total volume of wood in the central stem of trees ≥1.0" DBH, from ground line to the tree tip.	Douglas fir, ponderosa pine, true fir, Engelmann, and other spruces, lodgepole pine, other western softwoods, cottonwood, and aspen, and other western hardwoods
Woodland	The total volume of wood and bark in trees ≥ 1.5" DRC, from the DRC measurement point(s) to a 1.5-inch top diameter, including branches that are at least 1.5" in diameter along the length of the branch.	Woodland softwoods and woodland hardwoods

The FIESTA package enabled the customization of numerous filters tailored specifically to the Colorado context. This includes filtering for forested counties in Colorado, excluding those with a standard error greater than 25% and assessing only non-reserved land, though state land was included. Further, we filtered for standing dead trees, and only those which are hard (salvable) dead. This includes dead trees that have less than 67% of the volume cull due to rotten or missing cubic-foot volume loss [170].

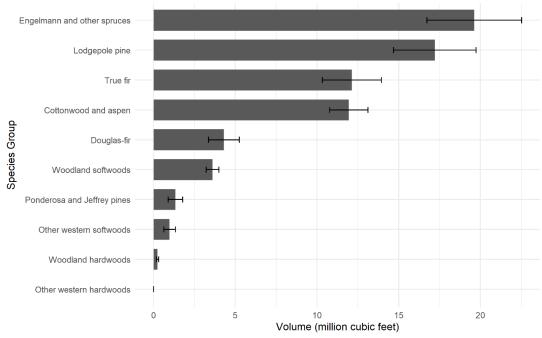


Figure 10. Statewide salvageable volume by species group with 95% confidence intervals. The bar plot displays the estimated volume (in million cubic feet) for different species groups, with error bars indicating the 95% confidence intervals for each estimate.

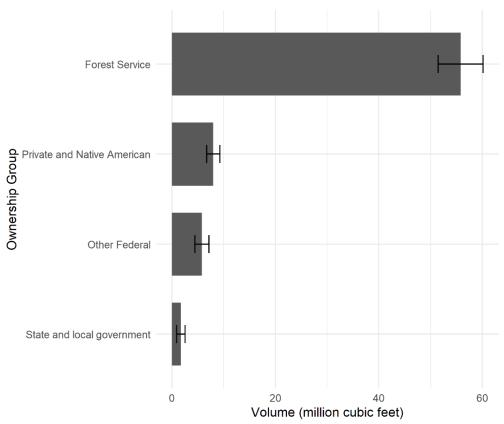


Figure 11. Statewide salvageable volume by ownership group with 95% confidence intervals. The bar plot displays the estimated volume (in million cubic feet) for different ownership groups, with error bars indicating the 95% confidence intervals for each estimate.

Results and Discussion

The total salvageable material (less than 67% of the volume cull due to rotten or missing cubic foot volume loss) in Colorado's nonreserved lands is 7,997,960,153 hundred cubic feet (CCF) (7,140 million cubic feet (MCF) or 7.14 billion cubic feet (BCF)). Englemann and other spruces and lodgepole pine species groups have the most salvageable material (196,209 +/- 14,810 CCF and 172,107 +/- 12,876 CCF respectively; **Figure 10** and **Table D2**). Across ownerships, 78% of the material on nonreserved lands is on U.S. Forest Service land (558,252 +/- 22,193 CCF; **Figure 11** and **Table D3**). The actual biochar yield from this volume is dependent on the thermochemical conversion technology but is estimated to yield approximately 1,999,490,038 CCF of biochar.

Limitations

This analysis uses the most up to date FIA data available in Colorado, which is up to 2019. To include a full 10-year cycle of data, we used data from 2010-2019. Thus, this may not represent current conditions on the landscape. Many severe disturbances have occurred in Colorado since 2019, including the 2020 wildfire season and ongoing insect and disease outbreaks. The amount of standing dead material is likely higher than what is estimated here. Further, these estimates do not account for timber tree components such as bark and branches. Due to its spatial scale, this analysis is not meant to inform stand-scale or project-level forest management. However, it can be used to inform statewide and landscape-level planning and prioritization and provides enough information to determine that the amount of biochar that could be made from woody biomass in the state far exceeds the needs for the plugging of orphaned wells.

Task (3)(a)(VIII)

Examine whether the use of biochar in the plugging of oil and gas wells is consistent with the state's short-term and long-term greenhouse gas and pollution reduction goals, as set forth in section 25-7-102 (2)(g), taking into consideration the emissions of greenhouse gases and other pollutants caused by the production of biochar and the use of biochar in the plugging of oil and gas wells

Plain Language Summary

A comprehensive life cycle assessment (LCA) was performed which assessed GHG emissions with and without woody biochar. The functional unit was the plugging of one vertical well of a depth of 6800 ft. The LCA included all stages: biomass transport, pretreatment, thermochemical processing, biochar application, and standard well plugging inputs and outputs.

Different biochar production methods were evaluated, including stationary systems like auger reactors, rotary kilns, and batch reactors, as well as portable systems like retorts and mobile carbonizers. Each method's emissions and energy use were analyzed. Emissions associated with well plugging range from 0.64 to 6.11 tonnes CO_2e per well plugged, depending on the biochar production method, compared to 11.4 tonnes CO_2e per well plugged without biochar.

Considering there are currently 33,000 abandoned and unplugged wells in Colorado, if each well is plugged using 4.2 tonnes of biochar, emissions would be reduced from 11.4 tonnes CO₂e to 2.4 tonnes CO₂e per well, on average. Without biochar for plugging wells, emissions would be 374,580 tonnes CO₂e, but with biochar, emissions would be reduced to 77,770 tonnes CO₂e. By 2050, plugging every orphan well with biochar would result in a GHG reduction of 296,810 tonnes CO₂e, accounting for approximately 1.5% of the 2005 emission levels associated with the oil and gas industry.

Methodology

A cradle-to-grave life cycle assessment (LCA) was conducted using OpenLCA software based on ISO 14040 standards [174, 175]. Emissions data were sourced from Ecoinvent 3.9.1 and quantified using Global Warming Potential (GWP) with the U.S. Environmental Protection Agency's Tool for Reduction and Assessment of Chemicals and Other Environmental Impacts (TRACI) version 2.1 [176].

The goal and scope of this LCA was to evaluate the impact of sequestered carbon in woody biochar on the GHG emissions associated with the well plugging process. The LCA was evaluated with and without biochar use to understand the impact of biochar on the well plugging process. The functional unit for the system is the plugging of one vertical well (6800 ft).

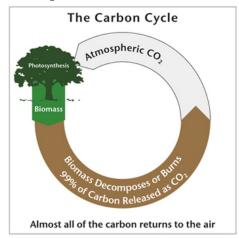
The LCA system boundary of biochar production included the following activities: biomass transport, biomass pretreatment (chopping, drying), thermochemical processing of biomass (dependent upon biochar scenario), biochar transport, and biochar application to the well with associated direct carbon sequestration. The LCA system boundary for the well plugging process included the following activities: roundtrip transportation of equipment/materials to well site, fuel required for equipment use at well site, and material inputs required for the process. The fabrication of machinery was not included in the system boundary.

The carbon sequestration from biochar utilization was calculated by multiplying the carbon content in biochar and biochar stability factor (**Equation 2**) which were dependent on the thermochemical conversion method [67]. The carbon sequestered in biochar originates from biomass, which captures atmospheric CO₂ through photosynthesis (**Figure 12**). Given the well is permanently sealed during the P&A process, a 100% permanence factor was considered.

Equation 2: Calculation formula for biochar carbon sequestration [4].

$$E_{stored} = Q_{biochar} \times C_{org} \times F_p^{TH} \times \frac{44}{12}$$

Where $Q_{biochar}$ is the quantity of biochar generated, C_{org} is the organic carbon content of biochar, F_p^{TH} is the permanence factor over a time horizon TH, and $\frac{44}{12}$ is the molecular weight ratio of CO_2 to carbon.



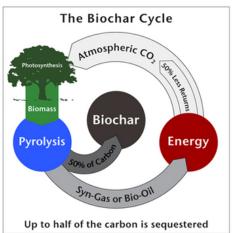


Figure 12. The carbon cycle of biochar. Biochar sequesters carbon by starting with biomass absorbing CO_2 from the atmosphere through photosynthesis. The biomass is then subjected to pyrolysis, converting it into stable carbon-rich biochar. [177]

The feedstock material used is forest harvest residue. All management and harvesting activities were excluded from the LCA [178]. After the biomass is collected, it is transported as whole logs to the pyrolysis facility for further processing if needed. A roundtrip transportation distance of 100 miles to the biochar production facility is estimated [179]. Once the biochar has been produced, it is assumed to be transported in bulk over a roundtrip distance of 115 miles [155].

Various biochar production methods were evaluated to represent the majority of production scenarios currently used in the biochar industry [180]. The emissions and impacts from processing are allocated to the biochar on a mass allocation basis, as multiple products are generated from pyrolysis. The syngas is recycled for heat at a 75% efficiency used in the drying process (where applicable) and the pyrolysis process [181]. Features and general assumptions for each of the varying biochar production methods are as follows:

1. Stationary System, Auger Reactor: The auger reactor is a cylindrical tube with an internal screw (auger) that moves biomass continuously through the system by the rotating auger.

The feedstock is reduced in size and dried in an industrial rotary dryer, lowering moisture content from 30% to 10% [51, 182]. Size reduction is done using a hammer mill. The process operates continuously at 500°C, with indirect heating and an inert nitrogen atmosphere [183, 184]. Electricity and natural gas are used for operation including powering the injection auger [182].

- 2. Stationary System, Rotary Kiln Reactor: The rotary kiln reactor is a cylindrical, long tube that rotates on its axis with a continuous feed and discharge of biomass. Similar to the auger reactor, the feedstock is reduced in size and dried in an industrial rotary dryer. Size reduction is done using a hammer mill. The process operates continuously at 500°C, with indirect heating and an inert nitrogen atmosphere. Electricity and natural gas are used for operation.
- 3. Stationary System, Batch Reactor: The batch reactor is a cylindrical vessel that handles biomass feed in batches. Similar to both the auger and rotary kiln reactor, the feedstock is reduced in size using a hammer mill and dried in an industrial rotary dryer from 30% moisture to 10% moisture [51, 182]. The process operates at 500°C, with indirect heating and an inert nitrogen atmosphere. Electricity and natural gas are used for operation.
- 4. Portable System, Retort: The pyrolysis process at a temperature of 550-600°C uses portable kilns operated with propane and diesel for start-up [161]. Biomass is air-dried to 20% moisture content, as portable retorts can handle higher moisture levels, eliminating the need for pre-processing drying [53]. The biomass is reduced in size using a diesel-powered medium chipper [185].
- 5. Mobile System, Carbonizer: Key parameters for the mobile carbonizer are based on air curtain burner systems like the CharBoss [185]. No drying is needed, as the system handles higher moisture content biomasses, allowing air drying to 25% moisture content. Grinding or chipping is unnecessary. An excavator loads the material, and the batch process uses a diesel-powered blower. Propane is used for start-up, with pyrolysis occurring at 680-750°C.

Several companies are at various stages of developing small to large-scale biochar slow-pyrolysis units. However, detailed process data from these facilities are not available, as the units are still under development and the data is often kept confidential. Input data, including energy and fuel usage for the pyrolysis systems, as well as biochar organic carbon content and yield, which determine the carbon sequestration potential, are based on an extensive literature review and communications with biochar production facilities (**Table E1**).

For the well plugging process without biochar, the standard well plugging system served as the foundation for the LCA. This standard system's inputs and outputs were derived from a detailed techno-economic analysis. Key components of the process included the transportation of equipment to the well site, the use of fuel to power the equipment, and the use of materials such as cement, water, and bentonite, which are essential for plugging wells. See Task (3)(a)(VI) for additional details.

Results and Discussion

The total value of GHG emissions and reductions on a tonnes CO₂e basis per well plugged is presented in **Figure 13**. For a vertical well with no biochar, the total emissions are 11.4 tonnes

 CO_2e per well plugged. All biochar scenarios lead to a reduction in emissions, with adjusted totals ranging from 0.64-6.11 tonnes CO_2e per well plugged depending on thermochemical conversion method of the biomass.

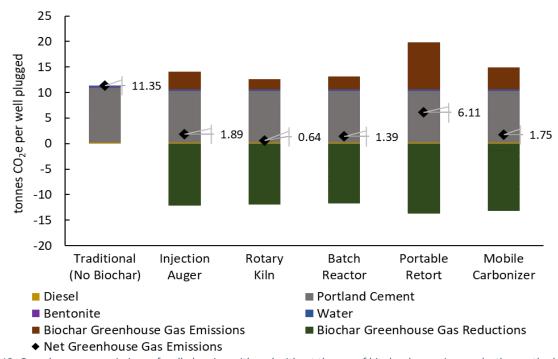


Figure 13: Greenhouse gas emissions of well plugging with and without the use of biochar by varying production methods. Black marker represents net greenhouse gas emissions.

Portland cement is the largest contributor to emissions in standard well plugging operations, accounting for 96% of the overall GHG emissions. This aligns with established knowledge that cement is one of the largest anthropogenic contributors to GHG emissions [186]. Diesel is the second-highest contributor, representing 2% of the total, primarily due to its use in transportation and equipment operation at the well site.

Carbon sequestration values and net GHG emissions for all five production methods is shown in **Table 9**. Despite the portable retort producing biochar with the highest carbon content and lowest moisture content—resulting in the greatest carbon sequestration —it also has the highest emissions due to the significant amounts of diesel and propane required for start-up. Consequently, it has the lowest impact on reducing GHG emissions.

The mobile carbonizer exhibits emissions comparable to all stationary systems but produces biochar with higher carbon content, resulting in greater sequestration values and the highest net negative emissions for biochar production. The three stationary systems—injection auger, rotary kiln, and batch reactor—show similar emissions and reductions due to their comparable preprocessing methods and energy requirements. However, the injection auger method has slightly higher production emissions than the rotary kiln and batch reactor due to additional electricity needed for the injection auger. The batch reactor has slightly higher emissions than the rotary kiln because of the greater energy needed for its start-stop operation, whereas the rotary kiln operates continuously [52].

Table 9: Carbon sequestration values and net greenhouse gas emissions for the varying biochar production methods.

	Injection Auger	Rotary Kiln	Batch Reactor	Portable Retort	Mobile Carbonizer
Total Greenhouse Gas Emissions Reductions (t CO₂e /well plugged)	-8.71	-9.96	-9.21	-4.49	-8.85
Greenhouse Gas Emissions Reductions Attributed to Spacer Fluid (t CO ₂ e /well plugged)	-8.00	-9.15	-8.46	-4.12	-8.13
Greenhouse Gas Emissions Reductions Attributed to Cement Mixture (t CO₂e /well plugged)	-0.71	-0.81	-0.75	-0.36	-0.72
Stable Carbon (t CO₂e/t biochar) (Excluding production emissions)	-2.87	-2.82	-2.77	-3.22	-3.10
Biochar Production Greenhouse Gas Emissions (t CO ₂ e/t biochar)	0.82	0.47	0.60	2.16	1.02
NET Greenhouse Gas Emissions Reductions (t CO₂e/t biochar)	-2.05	-2.35	-2.17	-1.06	-2.08

In terms of carbon sequestration, the injection auger reactor shows slightly higher values due to its higher carbon content compared to the rotary kiln and batch reactors. This difference could be attributed to the more extensive literature available for optimizing biochar production from an injection auger compared to the other reactors. Additional studies on optimizing biochar

production and quality for these three methods could strengthen their standing within the biochar production community. Overall, the differences between stationary reactors are minimal, and all are effective technologies for biochar production. However, given that the rotary kiln operates continuously and does not require electricity for an auger to move biomass through the reactor, it may have the most potential among the stationary systems.

There is higher uncertainty with the portable retort and mobile carbonizer, as these are newer and more innovative technologies with limited data and literature available [179]. Additionally, the effect of removing forest residues on the forest's above and below-ground carbon stocks is not included in this analysis. Further research is needed to understand the net impacts of increased removal of residues from forestry systems for biochar feedstock. This removal could reduce the risk of forest fires, alter productivity, or result in a loss of soil nutrients and carbon, potentially negatively affecting the forest ecosystem's productivity [187, 188]. Ultimately, the efficiency with which carbon in the biomass is converted to biochar will determine the climate offset potential that is realized.

Colorado has established a comprehensive strategy to mitigate climate change and transition to a sustainable energy future by setting GHG reduction goals for both the short and long term. These goals are based on 2005 GHG emissions levels of 140 million metric tons of CO₂e. To address these emissions, Colorado has set the following reduction targets that include a 50% emission cut by 2030, a 75% cut by 2040, and achieving net-zero emissions by 2050 [189].

The oil and gas industry, the third-largest source of GHG emissions in Colorado after electricity generation and transportation, plays a crucial role in the state's transition to a sustainable energy future. In 2005, oil and gas contributed 14.4% to the overall state GHG emissions [190]. Regulating the extraction and treatment of oil and gas is crucial for achieving Colorado's ambitious GHG emission reduction targets. Orphan well plugging is a critical operation that typically requires substantial amounts of cement, which contributes significantly to GHG emissions. Reducing the emissions associated with well plugging can effectively lower the overall GHG footprint of the oil and gas industry.

Considering there are currently approximately 1,000 orphaned wells in Colorado, if each well is plugged using 4.2 tonnes of biochar, average emissions would be reduced from 11.4 tonnes CO₂e to 2.4 tonnes CO₂e per well, considering both the emissions and reductions of biochar. Plugging all the orphaned wells would result in a GHG reduction of 8,994 tonnes CO₂e, or a 0.04% decrease in 2005 emissions levels attributed to the oil and gas industry. If all of the 33,000 unplugged and abandoned wells in Colorado [191] equivalent to an annual removal of 65,000 cars from the road [192].

Task (3)(a)(IX)

Determine whether the use of biochar when plugging an oil and gas well:

- (A) Could, with verified net permanent removal of atmospheric carbon as established to internationally recognized standards, allow an operator or other person plugging an oil and gas well to receive legitimate carbon credits or offsets
- (B) Would require any changes to state law to allow the use of biochar in the plugging of an oil and gas well or to allow a state agency to coordinate with applicable federal agencies and other agencies in the implementation of the pilot program
- (C) Would comply, in the case of plugging an oil and gas well owned by the United States or a tribal land trust, with federal law or any other applicable law

Plain Language Summary

Our findings indicate that biochar is a promising material for carbon sequestration and GHG emissions reduction. Biochar incorporation into plug and abandonment (P&A) operations creates a permanent carbon sink, as long as the well is not destroyed or decomposed. Therefore, the use of biochar in well plugging could allow an operator to receive carbon credits or offsets. Agencies within the voluntary carbon market currently do not award carbon credits for biochar's use in well plugging, but it is likely that methodologies will be developed soon, making it a viable option in the future. However, biochar is not explicitly mentioned in any existing state or federal legislature related to oil and gas well maintenance or plugging, and would require a variance for use or be added to the list of approved materials for P&A.

Using biochar for carbon credits or offset

Biochar, a carbon-rich material produced from biomass through pyrolysis, has significant potential for carbon sequestration and reducing greenhouse gas emissions. In the voluntary carbon market, biochar producers can sell carbon removal credits by enrolling in recognized third-party certification systems. Various agencies, including Puro.earth, Gold Standard, and Verra, issue these carbon credits in the U.S. [7]. All greenhouse gases emitted during the cultivation of biomass, the pyrolysis process, and up to the packaging of biochar are recorded and the carbon sink potential of biochar is determined by the amount of carbon it contains, minus the carbon expenditure of its production.

When used in construction materials as a sand substitute or additive in asphalt and plastics, biochar acts as a carbon sink for the lifespan of the material. Carbon is only released back into the atmosphere if the material is disposed of, destroyed, or decomposed, thereby losing its carbon sink status [4]. Incorporating biochar into well-plugging materials like cement and water can create a permanent carbon sink, provided these materials remain stable.

As the biochar industry is relatively new, regulations and standards for labeling and certifications are still developing. Currently, there are no specific regulations for using biochar in orphan well plugging. However, due to the permanent nature of the well-plugging process, both the use of biochar in the cement slurry and in the spacer fluid has the potential to generate carbon credits.

Well Plugging Costs with Carbon Credits (USD/tonne CO₂e)

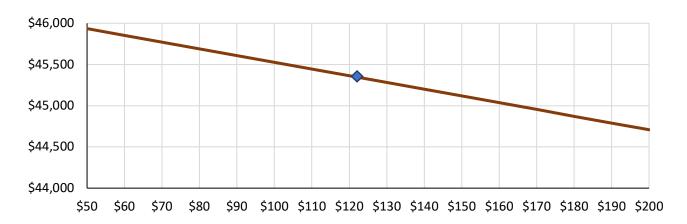


Figure 14: The impact of varying carbon credit values (in USD per tonne of CO_2e) on the total cost of well plugging. The break-even point, marked by a diamond, is at \$121 per tonne of CO_2e .

The prices for carbon credits of biochar are variable. As of February 2024, the average price was around \$150 per tonne of CO_2e [36]. Given that 4.2 tonnes of biochar are used in a standard well-plugging operation, this would generate 7.5 tonnes of carbon sequestration potential. **Figure 14** illustrates the range of potential value of the carbon credits in a standard well-plugging operation, varying from \$50 per tonne of CO_2e to \$200 per tonne of CO_2e [35, 36]. A price of \$121 per tonne of CO_2e would be required to break even on the added cost of biochar, assuming the credits are allocated to the well operator.

Compliance with existing legislation

Biochar represents a viable solution for long-term carbon sequestration in oil and gas wells, but the contemporary nature of this solution has inhibited its incorporation into existing legislature. While there are no direct regulations, on a state or federal level, that explicitly banned the use of biochar in P&A operations, it is likely not considered a "normal" component of filler material or cement mixtures. Therefore, a special approval or change in the rules would be required in order to use biochar for P&A in a case-by-case scenario. Additional legislation would likely be required to implement the incorporation of biochar into P&A operations on a large scale. See task (3)(a)(II) for additional details.

Conclusions and Future Recommendations

Unplugged oil and gas wells have been associated with the migration of gases and fluids, potentially increasing greenhouse gas (GHG) emissions such as methane and the risk of groundwater contamination. During plug and abandonment (P&A), several cement plugs are placed into strategic locations in the wellbore to isolate the reservoir and other fluid-bearing formations. While cement plugs are considered to be a long-term or permanent solution, they are also susceptible to cracking under some circumstances. Under these conditions, gases and fluids would again be able to migrate outside of the wells, with plugged wells in the United States emitting an average of $1.6 \text{ g CH}_4/h$ [9].

We conducted literature reviews, experimental analyses, life cycle analysis (LCA), and technoeconomic analysis (TEA) to determine the viability of using biochar as a filler material in between cement plugs and as a cement additive to 1) offset GHG emissions and sequester carbon and 2) improve cement durability, defined as results equal to or better than the compressive strength of non-amended cement. In addition, we reviewed relevant geochemical models and calculated the amount of woody biomass available in the state. The literature review highlighted that biochar can be produced from many different feedstocks using a wide variety of methods. For carbon sequestration purposes, woody feedstocks pyrolyzed at 450 and 600°C are of particular interest due to high %C in the final biochar product. However, a review of state and federal legislation related to P&A revealed that the use of biochar for well plugging is currently prohibited and would require an exception.

Laboratory experiments were conducted to determine the compressive strength of biochar-cement mixtures ranging from 0-10% biochar addition by weight. Early results indicated that cement mixtures including 5% and 10% were not suitable for use, and further studies were conducted with a maximum of 3% biochar added. The biochar-cement mixtures (and non-amended Portland cement) were analyzed for changes in compressive strength, chloride-ion penetration, sulfate attack, curing under high heat, and exposure to produced water from biochar incorporation. Collectively, the lab results revealed that a 3% addition of biochar to cement pastes yields promising results, although further testing is required under increased temperature and pressure scenarios, as these could not be accurately simulated during the first stage of testing. To test curing at high temperatures, we recommend a water tank method in which steel molds are placed in a hot water bath at 60-80°C [193-195]. For curing at high pressures, we recommend a triaxial cell, which is specifically designed to test cements used in oil wells [196]. Finally, we recommend a project hazard analysis improve confidence in biochar as a filler material between cement spacers. Existing concerns are that the biochar-water slurry may not have an adequate density to keep the cement plugs at the surface, which would not allow for effective well plugging.

From the combined LCA and TEA, we have determined that incorporating 15% biochar in the spacer and 3% biochar in the cement would result in a \$983 increase and reduction of 11.4 tonnes CO_2e for well plugging without the use of biochar to 0.64-6.11 tonnes CO_2e per well plugging with the use of biochar. Plugging the approximately 1,000 orphaned wells in Colorado with biochar would result in a .04% reduction in the 2005 baseline emissions attributed to O&G but expanding the use of biochar to include all currently abandoned wells (approximately 33,000) would results in 1.5% decrease in emissions. Current estimates for Colorado indicate that

approximately 413,320,500 tonnes of biochar could be produced from woody biomass, well exceeding the 138,600 tonnes of biochar needed to plug every well. Assuming carbon credits of \$121 per tonne of CO_2 or higher, using biochar in P&A operations would be economically feasible and could be sourced entirely from within the state. Based on the results of our research pertaining to HB-1069, we have developed go/no go decision markers developed to guide decisions to continue with or abandon project development, summarized in **Table 10**.

Based on the findings described in **Table 10** we believe that biochar has the technical and logistic potential to be implemented in well plugging resulting in a decreased carbon footprint of the oil and gas extraction without adding a financial burden. Plugging of orphan wells will also help prevent emissions of toxic gasses and fluids. A pilot scale experiment must be designed and executed to fill the remaining knowledge gaps and confirm the data presented in this assessment report, which should include the monitoring of wells plugged with biochar to determine their ability to mitigate contaminants.

Careful consideration should be taken when selecting biomass feedstock for biochar production to ensure the local community is not negatively affected. This includes evaluating the potential health risks associated with contaminants such as heavy metals and pathogens, which can be present in feedstocks like biosolid sludge and animal waste [197]. Additionally, the impact of odors and emissions from the production process on local air quality should be assessed. High-VOC biochars can pose health risks in extreme cases, as assessed by guideline values. However, most biochars typically sorb rather than release VOCs [198]. This finding highlights the importance of monitoring VOC concentrations in biochar after production and before application. It is also important to address community concerns and perceptions, as the use of waste materials can carry a stigma. Ensuring proper handling, processing, and communication about safety measures can help mitigate these issues and support community acceptance. Future studies on using biochar for well plugging should incorporate evaluations of both GHG and non-GHG emissions from biochar production and storage to assess their impact on local communities where production takes place, as this aspect was beyond the scope of the current report.

Table 10. Project Go/No-Go (G/NG) Decision Point(s)

G/NG Description	How would you demonstrate completion?
Biochar-cement composite maintains integrity	Compressive strength under various scenarios (e.g. increased temperature and pressure) must be equal to or greater than non-amended cement Specific parameters to be evaluated include amount of biochar that can be added, chloride ion penetration, sulfate attack, and compressive strength following curing at high temperature and pressure. Preliminary data supports the addition of biochar to cement, although heat studies have not been completed yet.
Biochar incorporation to P&A efforts offsets sufficient carbon	Considering most of biochar is stored in the spacer, integration into well plugging spacer provides proper clearance and effective displacement of fluids inside the well.
Filler material integrity	Project hazards analysis is completed and does not indicate increased risk associated with the use of biochar between cement spacers
Commercial viability	Carbon capture credits are high enough to offset the additional costs associated with using biochar (minimum \$121 per tonne CO ₂ , with credits allocated to the well operator) ¹²
Legislative requirements	Variance is granted by the Colorado Energy & Carbon Management Commission and the Bureau of Land Management
Sufficient biomass exists to produce enough biochar	Estimate woody biomass in the state of Colorado and approximate how much biochar could be produced from that amount. The amount of biochar needed to fill all orphan wells in the state of Colorado is below the estimated amount of biochar that could be produced from woody biomass in the state. Current estimates indicate that there is enough woody biomass to be used for P&A operations.
Environmental justice considerations	Potential community impacts from biochar production emissions, including non-GHG emissions associated with biochar production are considered. Air quality monitoring is suggested. Community outreach and engagement from the biochar production community and any community in the vicinity of wells plugged with biochar should be incorporated into future plans.

¹² Prices updated May 2024

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Appendix A

 Table A1. Summary of experimental results of biochar-cement testing

Feedstock	Pyrolysis	Particle size (um)	Replacement	Findings	Reference
Poultry litter, rice husk, pulp paper mill sludge	450-500 C, 10 C/min	N/A	0-1%	Similar tensile strength	Akhtar and Sarmah, 2018 [90]
Rice husk waste	550 C	<300	0-8%	Slightly improved compressive strength, 5.8% flexural strength increase with 2 weight % replacement, 17.3% reduction in permeability at 5 weight %	Aneja et al., 2022 [81]
Rice husk waste, sugarcane bagasse	700 C, 10 C/min	<100	5-20%	5 weight % bagasse presented higher compressive strength, slight increase in tensile strength at 5 weight %; tensile strength lowered with further replacement	Asadi et al., 2018 [85]
Desert palm rachis	300-500 C, 10 C/min	<500	1-5%	Max improvement on flexural strength (5%) found at 1 weight %; 5 weight % slightly reduced flexural capacity	Boumaaza et al., 2022 [93]
Dewatered sludge	300-600 C, 10 C/min	<600	2%	5.8% increase in compressive strength, enhanced cement hydration process	Chen et al., 2020 [84]
Corn straw	300-550 C, 10 C/min	<100	1-5%	Permeability reduced, 14.7% GHGE reduction could be achieved	Chen et al., 2022 [65]
Wood saw dust	500 C	<125	0-5%	Comparable compressive strength to ultra-high performance concrete samples, reduced 72-h	Dixit et al., 2019 [82]

				shrinkage by 21% and 32% for 2 and 5 weight %, cement hydration accelerated	
Wood saw dust	300-500 C, 10 C/min	<400	0-5%	6-7.5% increase in 28-day tensile strength	Gupta and Kua 2018 [91]
Saw dust	500 C, 10 C/min	<200	0-5%	13% flow reduction	Gupta et al., 2018a [97]
Wood saw dust	300 C, 10 C/min	<50	0-2%	7-day and 28-day fracture energy improved, permeability improved, small amounts had little effect on flexural strength	Gupta et al., 2018b [96]
Woody biomass	500 C, 10 C/min	<200	0.5-2%	Reduction in flexural and tensile strength with increased dosage of biochar, optimal dosage is 1-2 weight %, max flexural strength gain at 0.5%	Gupta et al., 2020 [89]
Rice husk, wood waste	500 C, 10 C/min	<60	0-2%	Strength loss against sulfate attack reduced with 2 weight %, 120-day strength loss from chloride-ion penetration, biochar + silica provides better resistance to sulfate ion permeation	Gupta et al., 2021a [99]
Coconut shell, mixed tropical wood	400-450 C	<50	2%	Biochar can improve C sequestration capacity (esp. mix of coarse and fine), combination of finer and coarser fractions improved workability and enhances 3- and 7-day compressive strength	Gupta et al., 2022 [69]
Bagasse, wheat/pean ut/rice/coco nut	500 C, 10 C/min	<75	2%	Coconut husk reduced initial setting time by 26%, final by 14.2%, 18% increase in compressive	Javed et al., 2022 [63]

				strength with 2 weight % bagasse; higher amorphous silica = higher increase in compressive strength	
Sugarcane bagasse	400-500 C, 10 C/min	N/A	5-10%	Higher strength against sulfate attacks at 56 and 90 days at 5 weight %	Khan et al., 2021 [102]
Waste wood	500 C, 20 C/min	<1020	0-10%	1-3 weight % reduced chloride diffusion coefficient by 32%	Ling et al., 2023 [101]
Bamboo chips	650-750 C, 15 C/min	<200	0-4%	Up to 20% increase in compressive strength with 1 weight % replacement	Liu et al., 2022 [88]
Olive stone, rice husk, wood chips	500 C	N/A	0.5-4%	Up to 4 weight% replacement has comparable compressive strength and water absorption	Maljaee et al., 2021 [83]
Weedtree	600 C	<300	2%	Slightly increased compressive strength (3.4% with 2 weight %), autogenous shrinkage reduced by 16.3%	Mo et al., 2019 [80]
Waste synthetic eucalyptus plywood	500 C	<100	0-10%	Enhanced 28-day compressive strength by 6.5 weight %, slightly increased tensile strength	Qin et al., 2021 [86]
Rice husk	800 C, 6 C/min	<30	0-1%	13% increase in flexural strength for 2 weight %	Restuccia and Ferro 2016 [95]
Virgin woodchips	500 C, 10 C/min	<200	0-2.5%	1 and 1.5 weight % had 7% and 10% increase in flexural strength	Restuccia et al., 2020 [94]

Wood chips	400 C	<500	0-5%	10% flow reduction, 6% flexural strength improvement with 1 weight %, 5 weight % replacement is optimal; plasticizers can help with flowability	Sirico et al., 2022 [92]
Waste wood	500 C, 10 C/min	<100	1-8%	Increased compressive strength 8.4% for 2-3 weight % addition	Tan et al., 2022 [87]
Rice husk	450-550 C	<500	0-5%	8% flow reduction	Yang and Wang 2021a [98]
Rice husk	500 C, 10 C/min	<200	0-5%	Diffusion of chloride ion was reduced, less strength loss at 5 weight %	Yang and Wang 2021 [100]

Appendix B

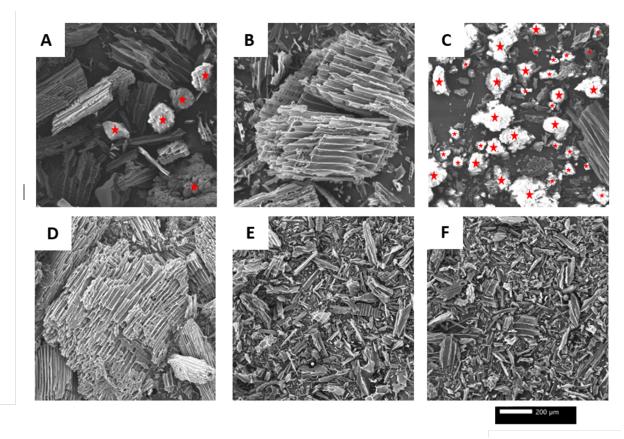


Figure B1: SEM images of the 6 biochar samples. A: BC1; B: BC2 (crushed); C: BC3; D: BC4; E: BC5; F: BC6. Inorganic contamination marked in red.

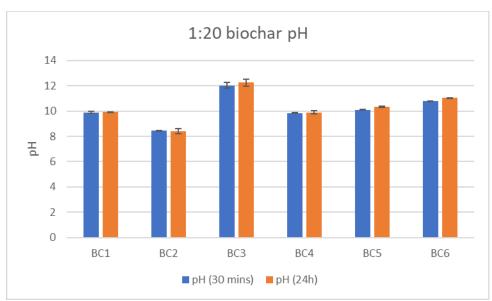


Figure B2: pH of all 6 biochar samples.

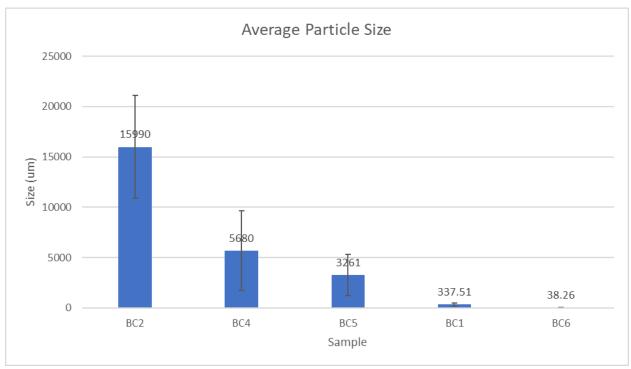


Figure B3: Average particle sizes of all 6 biochar samples before grinding

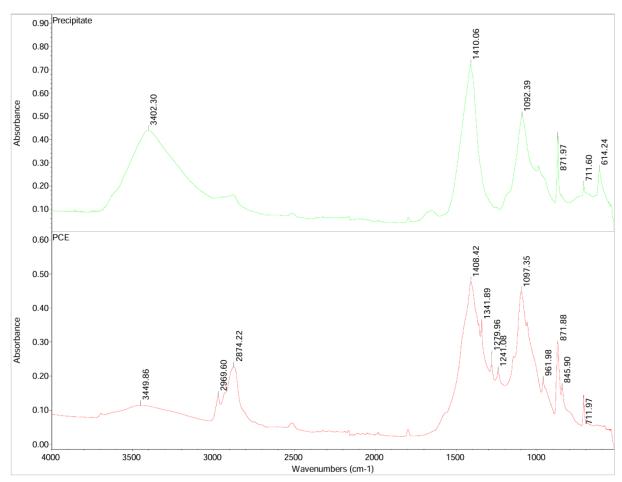


Figure B4: FTIR data of precipitate in water extruded by 5% sample after 28 days. Extreme similarity to pure PCE sample suggests PCE is a major constituent of this extruded water and was therefore added in excess.

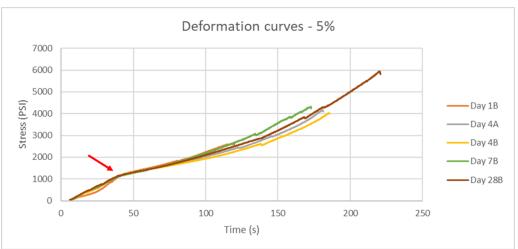


Figure B5: Deformation curves for 5% biochar compression tests. Note that these tests do not measure dimensional change and so a true Young's Modulus cannot be determined. 5% (S5E) failed gradually as seen in figure S6, and so the value reported is not the final value, but the point of plastic failure, marked with a red arrow. In these cases, the machine was not stopped by a sudden loss of pressure, but rather the sample cylinder had been compressed so small, the machine could no longer detect the sample at a certain pressure. These samples retained a lot of water and were compressed from 4 inches to 2 inches or less once broken. All other tests kept their 4-inch height even after cracking. The "best break" from the group broken that day is shown. Each mix and each time point contains 2-4 cylinders to pick the "best" plot from. Reported stress at break values are the 2-4 replicates averaged. Certain points were retested due to large error, poor breaks, or unclear trends. Additional stress curves available on request.



Figure B6: 3% mixtures using large particle size. Since no biochar was truly mixed in to the cement, these tests were discontinued.

Isotherm Log Absolute Plot

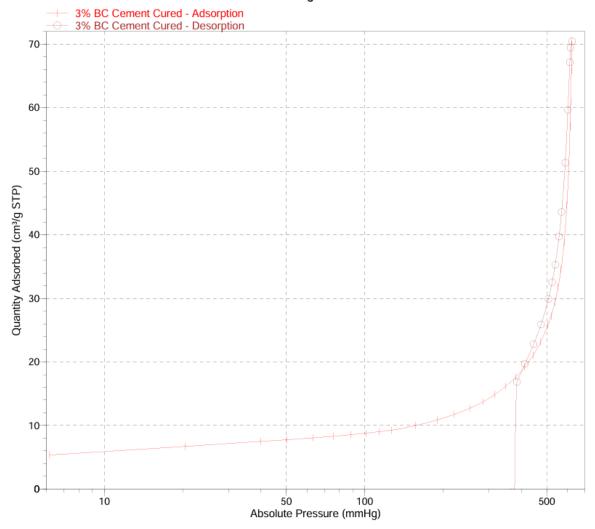


Figure B7: Sorption isotherm generated during BET analysis of 3% biochar-cement sample. Cement was fully cured and broken into pea-sized fragments before analysis. See full BET analysis in appendix 1

Table B1: Major constituents in the produced water used for curing. Select organic and inorganic compounds were analyzed.

Name	Presence (ug/L)
	, 5, ,
Benzene	3216
Ethylbenzene	940
Naphthalene	970
Isopropylbenzene	265
1,3,5-trimethylbenzene	703
4-isopropyltoluene	134
toluene	5016
Total xylenes	6292
n-propyl benzene	462
1,2,4-trimethylbenzene	2401
Sec-butylbenzene	165
n-butylbenzene	158
Acetone	2211
Chloride	23814880
Nitrate	285320
Bromide	78370
Sulfate	112420
Total PAH	115.6

Appendix C

Table C2: Well Plugging Assumptions and Parameters Used in the Economic Analysis

Vertical
6800 ft
5 - 9 1/8 inches
6
11.6 tonnes (271 sacks)
4 workers
4 days
Bulk truck, triplex truck, workover rig
Pressure test, wireline, squeezing, well plug
placement, spacer placement, cut & cap
115 mi (roundtrip)
\$58-\$348/tonne, (Avg - \$209/ tonne)

Appendix D

Table D3: Individual tree species and corresponding species group codes

Common Name	Scientific Name	Species Group
Douglas-fir	Pseudotsuga menziesii	Douglas-fir
ponderosa pine	Pinus ponderosa	Ponderosa pine
white fir	Abies concolor	True fir
corkbark fir	Abies lasiocarpa var. arizonica	True fir
subalpine fir	Abies lasiocarpa	True fir
Engelmann spruce	Picea engelmannii	Spruce
blue spruce	Picea pungens	Spruce
lodgepole pine	Pinus contorta	Lodgepole pine
Utah juniper	Juniperus osteosperma	Pinyon-Juniper
Rocky Mountain juniper	Juniperus scopulorum	Pinyon-Juniper
oneseed juniper	Juniperus monosperma	Pinyon-Juniper
common or two-needle pinyon	Pinus edulis	Pinyon-Juniper
Rocky Mountain bristlecone pine	Pinus aristata	Other western softwoods
limber pine	Pinus flexilis	Other western softwoods
southwestern white pine	Pinus strobiformis	Other western softwoods
eastern cottonwood	Populus deltoides	Cottonwood and aspen
quaking aspen	Populus tremuloides	Cottonwood and aspen
Fremont cottonwood	Populus fremontii	Cottonwood and aspen
narrowleaf cottonwood	Populus angustifolia	Cottonwood and aspen
plains cottonwood	Populus deltoides ssp. monilifera	Cottonwood and aspen
boxelder	Acer negundo	Other western hardwoods
water birch	Betula occidentalis	Other western hardwoods
green ash	Fraxinus pennsylvanica	Other western hardwoods
curlleaf mountain-mahogany	Cercocarpus ledifolius	Woodland hardwoods
Gambel oak	Quercus gambelii	Woodland hardwoods

Table D2: Statewide salvageable volume by species

Species group	est_CCF	pse	CI95left	Cl95right
Other western hardwoods	3438	66.8804489	0	7944
Woodland hardwoods	246373	14.5623471	176054	316692
Other western softwoods	983447	18.4436772	627941	1338953
Ponderosa and Jeffrey pines	1339218	16.8583639	896716	1781719
Woodland softwoods	3607717	5.54201225	3215842	3999593
Douglas-fir	4303622	11.1387542	3364074	5243169
Cottonwood and aspen	11948222	5.01933408	10772790	13123654
True fir	12137525	7.56511514	10337852	13937199
Lodgepole pine	17210711	7.4813965	14687059	19734364
Engelmann and other spruces	19620920	7.54828614	16718129	22523711

Table D3: Statewide salvageable volume by ownership group

Ownership group	est_CCF	pse	CI95left	Cl95right
State and local	17625	23.2524209	9593	25657
government				
Other Federal	58234	11.8394329	44721	71748
Private and Native	79901	8.12833838	67172	92630
American				
Forest Service	558252	3.97545959	514754	601749

Appendix E

Table E1: Relevant properties of pyrolysis, biomass, and Biochar for the various thermochemical conversion methods

	Injection Auger [202- 204][27, 28, 29]	Rotary Kiln [34, 205, 206][26, 33, 34]	Batch Reactor [207- 210][25, 30,	Portable Retort [161][12]	Mobile Carbonizer [185][11]
	-	-	31, 32]		
Operating Temperature	500°C	500°C	500°C	550-600°C	680-750°C
C _{org} Content	80%	80%	76%	88%	89%
Biochar Yield	24%	38%	27%	16.5%	17%
Energy Used	Electricity Natural Gas	Electricity Natural Gas	Electricity Natural Gas	Diesel Propane	Diesel Propane