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Research Article

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Posted Date: August 13th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-799061/v1>

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Version of Record: A version of this preprint was published at Scientific Reports on February 21st, 2022. See the published version at <https://doi.org/10.1038/s41598-022-06374-6>.

**Sustainable Biopolymer Soil Stabilization in Saline Rich, Arid Conditions –
A ‘Micro to Macro’ Approach.**

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Abstract

Water scarcity in semi-arid/arid regions is driving the use of salt water in mining operations. A consequence of this shift, is the potentially unheeded effect upon Mine Tailing (MT) management. With existing stabilization/solidification methodologies exhibiting vulnerability to MT toxicity and salinity effects, it is essential to explore the scope for more environmentally durable sustainable alternatives under these conditions.

Within this study we investigate the effects of salinity (NaCl, 0-2.5 M) and temperatures associated with arid regions (25 °C, 40 °C), on Locust Bean Gum (LB) biopolymer stabilization of MT exemplar and sand (control) soil systems. A cross-disciplinary ‘micro to macro’ pipeline is employed, from a Membrane Enabled Bio-mineral Affinity Screen (MEBAS), to Mineral Binding Characterisation (MBC), leading finally to Geotechnical Verification (GV).

As predicted by higher Fe₂O₃ LB binding affinity in the MEBAS studies, LB with 1.25M NaCl, results in the greatest soil strength in the MT exemplar after 7 days of curing at 40 °C. Under these most challenging conditions for other soil strengthening systems, an overall UCS peak of 5033 kPa is achieved. MBC shows the critical and direct relationship between Fe₂O₃ LB ‘high-affinity’ at the molecular level and ‘high-strength’ achieved at the geotechnical level. This is attributed to biopolymer binding group’s increased availability, with their ‘salting-in’ as NaCl concentrations rises to 1.25M and then ‘salting-out’ at higher concentrations. This study highlights the potential of biopolymers as robust, sustainable, soil stabilization additives in challenging environments.

Keywords. *sustainability, sustainable engineering, micro to macro, soil stabilization, biopolymer, bio-mineral, mine tailings, water scarcity, sea water utilization.*

34 **Introduction**

35 Stabilization/solidification is used by engineers to improve the geotechnical characteristics of
36 soils for a range of purposes (slope stabilization, low carbon building materials, road/building
37 foundations). Ordinary Portland Cement (OPC), is typically added to soils in high quantities
38 (10% by weight), forming a homogenous, rigid microstructure, improving soils cohesive
39 strength properties.^{1, 2} The ability of OPC to improve soils strength has led to its global and
40 universal use for a huge range of building and geotechnical applications. Some of the largest
41 geotechnical structures are Mine Tailings (MT) dams, where waste from mining activity is
42 stored. These facilities are often gigantic in size, typically storing waste built up over decades
43 of mining operation. Using OPC to stabilises these vast structures presents very real
44 environmental issues. Notably OPC accounts for 5-7% of anthropogenic carbon dioxide
45 emissions with 1 tonne of cement = 1 tonne of CO₂.^{3, 4} In its production, OPC further consumes
46 huge quantities of resources, such as raw materials (limestone, clay and sand), water and
47 energy.^{5, 6} This is accompanied by emissions of SO_x, NO_x, toxic particulate matter, carbon
48 oxides, metals, hydrogen fluoride/chloride and carbon monoxide by cement production plants,
49 resulting in numerous local and global detrimental environmental effects.⁷ When these effects
50 are massively increased with the scale of MT structures.⁸ Furthermore there is growing
51 evidence that OPC does not offer optimum strengthening under the environmental conditions
52 MT dams operate.

53 Mining operations within arid/semi-arid regions account for up to 50% of major metal
54 production (Ag, Au, Cu, Pb, Zn).⁹ Due to low rainfall quantities (25 mm to 500 mm average
55 rainfall per year), high temperatures (up to 30-45 °C average) and the sheer size of mining
56 operations, water scarcity has become a major factor within these regions, Chile being a key
57 example.^{9,10,11,12} In order to relieve water stresses, mining companies have increasingly looked
58 towards the use of salt water. In coming years, it will therefore become critical that MT

59 stabilization/solidification additives are able to withstand highly saline conditions, as saline
60 operations become the new norm. When considering OPC stabilizations use within saline
61 conditions, limitations are found.¹³ Reactions between salt anions (Cl⁻) and cement matrices
62 cause the formation of voluminous, Friedls salt compounds, resulting in the expansion and
63 cracking of cements rigid microstructure, reducing soil strength over time.^{14, 15} The long term
64 use of OPC, to prevent MT failures within saline environments, is therefore untenable.

65 A lack of understanding of the detrimental environmental effects upon OPC, as well as the
66 increased financial and environmental costs of scaling up OPC, means more and more MT
67 dams are left un-stabilised and ultimately unsafe. When MT dams fail, it leads to catastrophic
68 humanitarian and environmental disaster. At least one major MT disaster occurs each year, for
69 example in 2019 a failure in Brumadinho, Brazil resulted in the release of 11.7 million m³ of
70 mining mud, causing at least 220 deaths and devastating environmental damage to over 600km
71 of the Rio Paraopeba.^{16, 17} Therefore, as a global community, we critically requires a more
72 sustainable, scalable alternative to OPC, that functions optimally under the range of
73 challenging environments found within mining facilities, with saline-arid conditions being a
74 principle environment of interest.

75 Chemical¹⁸, physical¹⁹ and biological²⁰ based approaches have been explored as sustainable
76 OPC soil stabilization alternatives. Biological based methodologies, such as microbial/enzyme
77 induced cementation (MIC/EIC), have attracted increasing attention due to desirable qualities,
78 such as; renewable, low carbon production, low toxicity and their increasing economic
79 viability.^{21, 22} However both microbial and enzymatic methods are severely affected by MT's
80 biologically hostile conditions, which is further exacerbated by increased temperatures and
81 salinity.^{23, 24, 25} Further exploration is therefore required to discover a more environmental
82 durable solution, with the ability to withstand highly saline conditions, whilst retaining the
83 sustainability benefits biological stabilization offers.

Biopolymers are polymers derived from natural sources. They can be divided into three major classifications; polynucleotides (e.g. DNA, RNA), polypeptides (e.g. proteins) and polysaccharides (e.g. carbohydrates). Our inspiration for using biopolymers in geotechnical engineering is: 1. low environmental impact; 2 sustainability; 3. non-toxicity and 4. low cost, typical of biological stabilization methodologies.²⁶ Polysaccharide additives in particular offer increased control and chemical versatility. Their ex-situ production, either through ex-cultivation or chemical extraction, providing control over quality, chemical composition and addition methodologies.²⁷ Polysaccharide additives have also been shown to exhibit a high stability when exposed to saline conditions, across a broad pH range and when stored for long periods of time.²⁸

In previous work we have introduced a ‘micro to macro’ methodology to assist in the rapid development of biopolymer soil stabilization additives.²⁹ At the microscale, Membrane Enabled Bio-mineral Affinity Screen (MEBAS) is a fast method to assess a large number of bio-mineral binding molecules. Mineral Binding Characterisation (MBC) can then be performed on a smaller number of candidates to help understand the micro-scale driving mechanism. Translating to the macroscale – Geotechnical Verification (GV) demonstrates how bio-mineral interactions at the molecular level result in macroscopic geotechnical soil property improvements.

This pipeline has shown the capability to identify ‘high-affinity, high-strength’ bio-mineral composites, showing how this binding affinity at the microscale directly translates into highly increased unconfined compressional strength (UCS) of the soil at the macroscale, MEBAS assessment is ~ 50 fold quicker, when compared to a typical trial and error ‘top down’ methodology.²⁹ The ability to rapidly identify, understand and verify suitable biopolymer additives dramatically catalyses progression in the field.

108 Here we build on previous research, utilising the MEBAS-MBC-GV pipeline to investigate the
109 effect of environmental conditions (salinity and temperature) through the micro and macro-
110 scales (Figure 1). Previously, the biopolymer Locust Bean Gum (LB) was found to vastly
111 strengthen a MT exemplar soil matrix (containing 10% Fe_2O_3).²⁹ Here we expand this work to
112 test the applicability of this biopolymer in a range of environments including in saline (0.5-
113 2.5M NaCl) and arid (25 °C, 40 °C) mining conditions, emulating environmental conditions
114 found for many MT facilities operating in water scarce regions. This study highlights the
115 potential of biopolymer additives as next generation, sustainable geotechnical solutions.
116

Results

Field System Selection

In this study, the effect of salinity/aridity on soil properties has been investigated through the micro and macro-scales, utilising MEBAS-MBC-GV methodology. Fe_2O_3 (abbreviated to Fe in sample names) was selected as the mineral of focus, due to its universal and consistence abundance in MT, and the relative activity of iron minerals within fresh MT material conditions.²⁹ The MT exemplar soil system (abbreviated to MT in sample names) is composed of SiO_2 (90% by weight, 90 – 150 μm) and Fe_2O_3 (10% by weight, 224 nm $\pm$ 119 nm) to emulate typical chemical and physical characteristics³⁰ found within real MT systems (Supplementary Table S1). Furthermore, surprisingly, little research has focussed on utilising abundant Fe minerals for soil stabilisation mechanisms. No soil organic matter was inputted, due to fresh MT material typically containing negligible organic contents.³¹ A pure sand (100% SiO_2) mineral control (abbreviated to C in sample names) system is also investigated from comparison.

Conditions typical of saline and arid environments were selected to simulate field conditions.¹⁰ As sea water contains a NaCl (abbreviated to S in sample names) concentration of 0.5 M, a concentration range of 0.5-2.5 M was selected due to the likelihood of elevated saline concentrations upon drying.³² For micro-scale experiments, all concentrations were diluted to avoid biopolymer viscosity effects. In order to keep the experiments equivalent, the ratio of LB:S was kept the same (see methods).²⁹ Micro-scale sample names have the addition of equivalent (eq.) to make this clear e.g. S0.5 – S2.5 eq. The GV experiments are cured at two different temperatures (25 and 40 °C) (abbreviated to T25 and T40 in the sample names). The list of sample names and their conditions are shown in Table 1.

MEBAS of Fe LB Binding Affinity in Saline Conditions.

In order to rapidly probe the bio-mineral binding intensities at the micro-scale, MEBAS was employed (Figure 2). For control experiments, LB exhibits an affinity to Fe particles, as previously identified.²⁹ Upon the addition of S0.5 eq. a significant increase in Fe LB binding intensity was observed (Figure 2A). When increasing salinity concentration further (S0.5-2.5 eq.), minor increases in binding intensity were observed. Figure 2B shows homogenous binding at all salt concentrations (S0.5-2.5 eq.), indicating the increased availability of Fe binding groups on the LB .

MBC of Fe LB in Saline Conditions.

MBC has been used to understand the changes in bio-mineral binding intensities (Figure 3). TGA was used to determine the quantity of organic coating on the mineral particle surface at different salinities, through combustion of the organic surface species. TGA thermal gradient profiles show the temperature at which particle coatings degrade, with the mass-loss directly attributed to the amount of biopolymer bound to the Fe surface (Figure 3A).^{33, 34}

The addition of salt shows a clear variation in the TGA profile, with a significant increase in mass lost observed up to S1.25 eq. (10.746%) (Figure 3B). When further increasing salinity (S2.5 eq.) a significant decline in mass loss was seen (10.746% to 6.256%), showing less coating, indicating less affinity at this higher salt concentration.

In this study ATR-FTIR is used to probe the effects of salinity on Fe LB chemical interactions associated with the adsorption of LB molecules at the bio-mineral interface (Figure 3C).³⁵

When LB molecules bind to the Fe surface, LB C-O-H absorption bands exhibit a wavenumber shift (1019 cm^{-1} to 1026 cm^{-1} and 1054 cm^{-1} to 1068 cm^{-1}) and an absorbance intensity drop, associated with formation of C-O-Fe bonds.

When introducing salt (S0.5-2.5 eq.) further reductions in absorption intensity and peak shifts were observed (1026 cm^{-1} to 1032 cm^{-1} and 1068 cm^{-1} to 1080 cm^{-1}), indicating the further conversion of C-O-H groups to C-O-Fe.

Zeta potential is a technique used to characterize surface charge at the solid/liquid interface and can probe the effects of LB coating and salinity upon the Fe surface (Figure 3D). The control sample (Fe) exhibits a negative charge of -63.81 mv. Upon addition of salt (S0.5 – 2.5 eq.), a reduction in negative surface charge was observed, with Fe S2.5 eq. exhibiting a charge of -26.786 mv.

LB coated Fe particles (Fe LB) displayed a significant reduction in negative surface charge, relative to Fe control sample (Fe LB = -10.696 mv compared to Fe = -63.81 mv). In contrast to the uncoated particles (Fe S0.5 eq. – Fe S2.5 eq.), when introducing salt to the LB coated particles (Fe LB S0.5 – 2.5 eq.), no significant change in surface charge was observed, indicating little change in surface electrostatics (Figure 3D).

GV of LB Stabilised Soils under Saline Conditions

To assess how this increased binding of LB to Fe particles in saline conditions translates to overall soil strength, GV was performed using an unconfined compression strength (UCS) tests, typically used for cohesive soils.

Relative to mineralogical controls (C (T25)), the addition of LB resulted in a significant improvement in UCS, increasing from 0 to 1828 kPa from C (T25) to C LB (T25) (Figure 5A). When salt is added, the UCS raises further, approximately doubling to 3713 kPa for C LB S0.5 (T25). However, this rise is independent of salt concentration with non-significant change in UCS upon further increased (Figure 5A).

190 For the MT soil system, addition of LB results in much greater increases in UCS compared to
191 controls (increasing from 0 to 3083 kPa from MT (T25) to MT LB (T25)) and notably, the
192 strength of MT LB (T25) is ~ 70% more than C LB (T25), attributed to the presence of Fe in
193 the MT system, which microscale analysis has shown to have high affinity for LB. As found
194 in the control soil system, on addition of salt, UCS rises, however, unlike the control system,
195 there is a concentration dependence. The UCS increases with increasing salt concentration,
196 peaking S = 1.25 M, with an UCS of 4510 kPa for MT LB S1.25 (T25). Further increases in
197 salinity (S2.5) resulted in soil strength loss (11%) (Figure 5A).

198 When considering curing at the higher temperature of 40 °C, an equivalent trend to
199 MT LB (T25) salt series was observed, with UCS peaking at 5032 kPa for 1.25 M salt
200 (MT LB S1.25 (T40)) (Figure 5B). While greater soil strength is achieved at this higher
201 temperature, it is notably that the decrease in soil strength at S = 2.5 M is also more dramatic.
202 There is a 48% loss of strength from MT LBS 1.25 (T40) to MT LB S2.5 (T40) compared to
203 an 11% loss at 25 °C from MT LB S1.25 (T25) to MT LB S2.5 (T25) (Figure 5B).

204 Interestingly, the C LB salt series show the same trend as the MT LB salt series at 40 °C with
205 the greatest UCS at S = 1.25 M. This is in contrast to the trend seen for the C LB salt series at
206 25 °C. However, the C LB (T40) salt series exhibits reduced UCS improvements compared to
207 the C LB (T25) salt series, with peak UCS of value of 2956 kPa for C LB S1.25 (T40), below
208 3000 kPa, while the C LB (T25) salt series all show values consistently above 3100 kPa
209 (Figure 5B).

210 For all C LB and MT LB samples, across both temperatures, on increasing salinity, an
211 increased axial strain at peak strength is seen (Supplementary Figure S3, S4). It is worth noting
212 that a negligible correlation was observed between UCS and both moisture retention and void
213 ratio for all LB stabilised samples (Supplementary Figure S3, S4) indicating a lack of suction
214 and densification effects upon soil strength improvements.

Discussion

When first considering mineralogical controls, MT and C show insubstantial strength characteristics (UCS = 0 -109 kPa). This is attributed to negative surface charges of SiO₂ (-75 mv³⁶) and Fe (-63.81 mv, Figure 3D), causing micro-scale particle repulsions and therefore a lack of cohesive strength on the macro-scale (Figure 5). When 1.25 M of salt are added, for both temperatures (T25, T40), small increases in UCS (30-215 kPa) are seen (Figure 5), ascribed to charge shielding effects of Na⁺, reducing negative repulsions (Figure 3D) and increasing cohesive interactions, as previously reported.³⁷

The salt series for all systems, with the exception of C LB (T25), displayed a trend of increasing UCS with increasing salt concentration up to a peak strength at 1.25 M, e.g. MT LB S1.25 (T25) (4510 kPa), MT LB S1.25 (T40) (5033 kPa) and C LB S1.25 (T40) (2956 kPa). For the MT series, MEBAS and MBC points to the strong affinity between the Fe surface and LB which is improved with salinity. An equivalent trend is seen in the TGA mass loss, with peak LB mass loss occurring at Fe LB S1.25 (Figure 3B). FTIR provides evidence of LB binding to Fe through C-O-H groups, initially upon the addition of Fe and furthermore upon increasing salinity (Figure 3C). Zeta potential shows that LB coating results in a significant reduction in surface charge, to within the threshold of aggregation (Figure 3D). Upon the introduction of salt (S0-2.5 eq.), no significant change in surface charge is observed, indicating little electrostatic contribution to increased Fe LB affinity in saline conditions. These results highlight that strength improvements for MT LB (T25) and MT LB (T40) samples are due to a combination of covalent and electrostatic bio-mineral interactions, as identified by our previous investigation.²⁹ Whereas, the further strength improvements observed under saline conditions are due exclusively to covalent based Fe LB bio-mineral interactions.

Previous studies have shown the micro-scale effects of salinity on non-ionic biopolymers such as LB, with low concentrations resulting in a ‘salting in’ effect.³⁸ The phenomena of ‘salting in’ is driven by the interaction of Na⁺ with hydrophobic hydroxyl groups, causing their increased polarisation and ability to be solvated by water molecules.³⁹ This results in the opening up of hydrophobic groups, increasing their ability to form high-affinity bio-mineral interactions (Supplementary Figure S5).

The loss of strength observed at highly saline conditions (S = 2.5 M) is postulated to be due to a combination of chemical and physical effects.^{38, 40} Chemically, highly saline conditions have previously been observed to cause a ‘salting out’ effect upon non-ionic biopolymer such as LB.³⁸ ‘salting out’ is an entropic effect caused by the ‘structure making’ characteristics of Na⁺ ions.⁴¹ Upon addition in high concentrations, Na⁺ dehydrates non-ionic biopolymer molecules such as LB, causing the reduced availability of binding groups for ‘high-affinity, high-strength’ bio-mineral interactions (Supplementary Figure S5), therefore lowering soil strengths.

Physical effects are also proposed to contribute to strength losses at higher saline concentrations. When examining soil samples a dramatic increase in efflorescence can be observed from S1.25 to S2.5 (Supplementary Figure S6), likely driven by phase separation in highly saline conditions. Although efflorescence is primary a surface aesthetic issue, the precipitation of salt within soil pores, known as sub-florescence, can cause crystallisation pressures, resulting in micro-cracking. Sub-florescence increases in smaller pores due to lower supersaturation thresholds, which may account for a proportion of the increased strength losses observed in MT samples.⁴⁰ The precipitation of large salt crystals is also likely to disrupt bio-mineral binding.

When considering the salt series of C LB (T25), peak UCS is observed for C LB S0.5 (T25) soil, with further increases in salinity resulting in little change (Figure 5A). Due to SiO₂'s highly charged nature, strength improvements are likely due to formation of non-specific electrostatic based bio-mineral interactions.^{42, 43} Increases in UCS, within saline conditions, are therefore postulated to be due to bio-mineral Na⁺ charge shielding effects.

When increasing curing temperature from T25 to T40, a number of strength trends are observed. Firstly, there is no significant difference seen in UCS, as a result of changing the temperature, for both C LB and MT LB soil systems, highlighting little sensitivity to arid-like environmental conditions and further reinforcing biopolymers potential use within higher temperature climates.²⁸ However, marked differences are seen when salt is present, with a more dramatic increase in UCS up to S1.25 and decrease for S2.5 within MT LB (T40) sample series compared to MT LB (T25) (Figure 5A, B). The more pronounced increase up to S1.25 and larger loss in strength for MT LB S2.5 (T40) is attributed to the entropic origin of both positive 'salting in' and negative 'salting-out' effects, resulting in increased energetic favourability at higher temperatures.

When comparing C LB (T40), with C LB (T25) salt series, strength improvements are attenuated (Figure 5B), with a UCS peak occurring for C LB S1.25 (T40). This phenomena is attributed to increasing SiO₂ negative surface charge, driven by the promotion of surface silanol group formation at higher temperatures (Supplementary Figure S7).³⁶ Increased negative surface charge is postulated to result in the dilution of Na⁺ shielding effects and weaker electrostatic, bio-mineral interactions. Fe surface charges are unaffected by temperature increases.⁴⁴ These results highlight the varying effects of curing temperature conditions when considering covalent (Fe LB) and electrostatic (SiO₂ LB) based bio-mineral interactions.

287 This study has highlighted a number of impactful and novel findings. The extension of
288 MEBAS-MBC, from identifying and understanding ‘high-affinity, high-strength’, mineral
289 binding molecules, to here probing the environmental conditions of solution salinity at the bio-
290 mineral interface, has further highlighted the power of the MEBAS-MBC-GV methodological
291 pipeline. With a rate of assessment over 50 times that of ‘top-down’ investigations, MEBAS
292 offers a simple and effective tool for investigating how environmental conditions may impact
293 the biopolymer additive use within a given soil system, before costly (time and resource),
294 geotechnical investigations.²⁹ Notably, the correlation between bio-mineral affinities at the
295 micro-scale (MEBAS-MBC) and macro-scale (GV) has been shown, further supporting the
296 finding that a high-throughput, cross-disciplinary approach can be employed to decode highly
297 heterogenous geotechnical soil systems.

298 This study has further reinforced the capacity of MBC to provide important micro-scale
299 information, helping to understand the chemical bio-mineral driving forces at the molecular
300 level that result in significant soil strength improvements. This understanding will allow for
301 the better design and optimisation of biopolymer additives in future studies.

302 Critically, this study has shown that unlike OPC and other biological stabilization
303 methodologies, where salinity and aridity cause detrimental effects, largely beneficial effect is
304 seen with LB biopolymers. This demonstrates the ‘saline compatibility’ of LB (and potentially
305 other biopolymer additives) indicating their potential future use to stabilise mining operations
306 that utilise sea water where water is scarce. It is noteworthy that globally 1 billion hectares of
307 soils have high salt concentrations, accounting for 7% of all land, showing applicability in these
308 soils too.^{45, 46} Further adoption of the powerful, systematic, MEBAS-MBC-GV methodological
309 pipeline, to investigate more diverse soil systems, should catalyse progression within the field,
310 unlocking the potential of biopolymers as next generation sustainable, chemical versatility and
311 environmental durable OPC alternatives.

Materials & Methods

Materials and Reagents. Locust Bean Gum (LB) and NaCl (S) was purchased from Sigma Aldrich/Merck and used without further purification. Sand (SiO₂) Fraction E (90-150 μ m) was purchased from David Ball sand specialists. Fe₂O₃ (Hematite) was acquired from Mineral Waters Ltd and used as supplied.

Biopolymer Solution Preparation. All LB solutions were prepared using the same methodology.²⁹ Powdered LB (MEBAS: 0.04 M, MBC: 0.01 M, GV: 0.2 M, Supplementary Figure S8) was first added to temperature controlled (40 °C), ultra-pure water and salt (S = MEAS: 0.1 - 0.5 M, MBC: 0.025 - 0.125 M, GV: 0.5 - 2.5 M) solutions, whilst simultaneously agitating with a magnetic stirrer (micro: 600 rpm, macro: 300 rpm). Concentration dilution was required when going from the macro-scale to the micro-scale to avoid biopolymer viscosity effects.²⁹ LB:S concentrations were maintained throughout to ensure macro and micro experiments were equivalent. Within each experimental section, concentrations prepared and their macro-scale equivalent conditions, which they are referred to throughout the study, are clearly outlined. Solutions were then incubated (10 minutes, 40 °C) and subsequently sonicated (10 minutes) using a VWR Ultrasonic water bath.²⁹

Membrane Enabled Bio-mineral Affinity Screen (MEBAS). MEAS was carried out using nitrocellulose (0.2 μ m pore size) membranes. 5 μ l drops of each prepared LB (0.04 M) solution was arrayed onto a nitrocellulose membrane in triplicate. After air drying, the membrane was submerged in a 3% wt/vol bovine serum albumin solution for 1 h to saturate any available nitrocellulose not covered by the arrayed LB. The membrane was then washed with ultrapure water before being subjected to an EDTA 10mM wash for 1 h to ensure any bound metal cations are removed.

Binding experiment solutions were then prepared (500 ml, S0 – aqueous solution, S0.1 – 2.922 g NaCl, S0.5 – 14.610 g NaCl). As previously outlined (biopolymer solution preparation), since LB:S is equivalent to macro-scale solutions, S0.1 - S0.5 are referred to as S0.5 - S2.5 eq. throughout this study. The pH was then adjusted to pH 7 using NH₄OH (0.5 M)/HCl (0.5 M) where necessary. Membranes were then subjected to a final wash using binding experiment solutions (50 ml, S0-2.5 eq., 5 times, 2 mins each). Fe (3 mg) particles were added to a solutions (50 ml). The resultant Fe suspensions were then sonicated (2 minutes, 8 kHz, 50:10 impulses). The prepared membrane was then submerged in the suspension for 4 h whilst rotating using a rotating using a Lab net Mini Labroller™. Following binding experiments, membranes were washed with fresh binding experiment solution (50ml, S0-2.5 eq., 2 times, 10 mins each). A Chemi-Doc gel documentation system (Bio-Rad, UK) was used to visualize and photograph the membranes and quantify the Fe binding intensities via densitometry.

Mineral Binding Characterization (MBC). LB (0.01M) solutions were first prepared (20 ml, S0 – aqueous solution, S0.025 – 0.029 g NaCl, S0.0625 – 0.073 g NaCl, S0.125 – 0.146 g). As previously outlined (biopolymer solution preparation), since LB:S is equivalent to macro-scale solutions, S0.025 – S0.125 are referred to as S0.5 - S2.5 eq. throughout this study. Fe (0.02 M, 64 mg) particles were then added and dispersed via sonication (10 mins, VWR Ultrasonic water bath).

The solution pH was then adjusted to pH 7 using NH₄OH (0.5 M)/HCl (0.5 M) where necessary. The solutions were then rotated for 30 minutes using a Lab net Mini Labroller™. Coated particles were separated using centrifugation (4000 rpm, 10 mins) and washed using ultra-pure water and saline (S0.5-2.5 eq.) solutions to remove excess non-bound biopolymers (4 repeats). Particles were then left to dry at room temperature, ready for analysis.

The mass of the organic particle coatings were determined using a PerkinElmer Pyris 1 Thermal Gravimetric Analyzer. Dry Bio-Fe particles were exposed to a temperature range of 20-800 °C under a 2/3 N₂, 1/3 O₂ atmosphere.

Surface functional groups were determined using a Perker Elmer Frontier Fourier Transform Infrared (FTIR) and Golden Gate Diamond Attenuated Total Reflection (ATR) spectrometer. Data collection and analysis was performed using Spectrum™ 10. Scans were made between 4000 cm⁻¹ and 400 cm⁻¹. Baseline correction was performed on all spectra.

Zeta potentials were determined using a Brookhaven BI-900AT. Fe and Fe LB particles were ground using a pestle and mortar and dispersed (0.01 mg/ml) via sonication (10 minutes, VWR Ultrasonic water bath) in control (S, 0.01M) and saline (S0.5 – 2.5 eq.) solutions. Micro-scale saline concentrations were employed for zeta measurements, as reproducibility issues were identified in macro-scale conditions (Supplementary Figure S9). This is attributed to the formation of polydisperse particle solutions, within highly saline conditions, due to Na⁺ charge shielding effects. Polydisperse solutions have previously been observed to cause the variation in zeta potential peaks and increased width at half heights, as seen within this study (Supplementary Figure S9), due to different sized particles resulting in heterogenous charge densities and Brownian motion effects.⁴⁷ The solution pH was adjusted to pH 7 using NH₄OH (0.5 M)/HCl (0.5 M), where necessary. Samples were scanned 5 times at 25°C and data analysed using Malvern ZetaPlus software.

Geotechnical Verification - Sample Preparation. GV preparation conditions optimisation can be found within a previous investigation.²⁹ LB (0.2 M, 27.5% (Mass_{water}/Mass_{soil}), corresponding to 1% Mass_{biopolymer}/Mass_{soil} addition) solutions, once prepared within saline (S0.5-2.5) and non-saline conditions, were immediately mixed with 160 g of material (MT and C) until a homogenous mix was achieved.

The resulting composite was then divided into 3 equal parts and compacted using a cylindrical drop hammer (2.1103 Kg, 246 mm × 37 mm) via 10, 126 mm drops, within a 202 mm × 42 mm hollow cylindrical sample mold. Samples were then extruded and left to cure (7 days at 25/40°C). All sample series were prepared and cured at the same time to ensure identical curing within each condition. 40°C curing temperatures were maintained using a temperature controlled Wykeham Farrance drying oven. Sample dimensions and masses were recorded to determine moisture retention and final densities.

Geotechnical Verification- Unconfined Compressional Strength Testing. A digital Tri-test ELE was used to perform unconfined compressional strength tests following the ASTM D2166 standard method.²⁶ A rate of displacement of 1.5 mm min⁻¹ was utilized throughout all testing. Load (N) and displacement (mm) data were collected during tri-axial tests. Sample bedding errors were removed pre-data analysis. The UCS (kPa) at failure of each sample was determined as the peak applied axial load (N), per cross sectional area. Axial strain (%) at peak strength was determined as the sample vertical displacement (mm) at failure as a proportion of the original sample height.

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517 **Figure 1.** A schematic representing a MEBAS-MBC-GV pipeline methodology. Field systems
518 are first investigated to determine experimental material properties. A simple, high throughput,
519 MEBAS is then carried out using the selected mineral, biopolymers and environmental
520 conditions. Geotechnical Verification (GV) is then performed to confirm micro-scale
521 observations. This process allows for the quick design of sustainable additive solutions for
522 stabilization/solidification. A secondary step using Mineral Binding Characterization (MBC)
523 is further outlined to both confirm binding observed via MEBAS and also understand the
524 binding mechanism associated with bio-mineral interactions.

525

		MEBAS - MBC		GV			
		Fe ₂ O ₃ (Fe)		SiO ₂ (100%) (C)		SiO ₂ (90%) + Fe ₂ O ₃ (10%) (MT)	
Temperature	NaCl (S)	-Ve Control	LB	-ve Control	LB	-ve Control	LB
25°C (T25)	0	Fe	Fe LB	C (T25)	C LB (T25)	MT (T25)	MT LB (T25)
	0.5	Fe S0.5 eq.	Fe LB S0.5 eq.	-	C LB S0.5 (T25)	-	MT LB S0.5 (T25)
	1.25	Fe S1.25 eq.	Fe LB S1.25 eq.	C S1.25 (T25)	C LB S1.25 (T25)	MT S1.25 (T25)	MT LB S1.25 (T25)
	2.5	Fe S2.5 eq.	Fe LB S2.5 eq.	-	C LB S2.5 (T25)	-	MT LB S2.5 (T25)
40°C (T40)	0	-	-	C (T40)	C LB (T40)	MT (T40)	MT LB (T40)
	0.5	-	-	-	C LB S0.5 (T40)	-	MT LB S0.5 (T40)
	1.25	-	-	C S1.25 (T40)	C LB S1.25 (T40)	MT S1.25 (T40)	MT LB S1.25 (T40)
	2.5	-	-	-	C LB S2.5 (T40)	-	MT LB S2.5 (T40)

Table 1. MEBAS-MBC-GV sample labels throughout the study.

Figure 2. Membrane Enabled Bio-mineral Affinity Screen (MEBAS) analysis of Fe LB binding within saline conditions (S0 - 2.5 eq.), at pH 7. A) Graph showing Fe LB binding intensities upon a salinity gradient (S0 - 2.5 eq.). B) Bio-Rad Chemi Doc membrane images of Fe LB within saline conditions (S0 - S2.5 eq.).

Figure 3. Mineral Binding Characterization (MBC) of Fe LB coated particles within saline conditions (S0 - 2.5 eq.) A) Thermal gravimetric analysis. Mass loss curves (% of total mass) upon a temperature change (25-800 °C). B) Total Mass loss (% of total mass) upon a temperature change (200-600 °C). C) ATR-FTIR of major region of interest C-O-H Bending (1200-800 ν). D) Zeta potential (mV) of Fe and Fe LB particles within saline (S0-2.5 eq.) conditions at pH 7.

Figure 4. Geotechnical Verification (GV). Macroscopic strength properties of C/MT LB S0 – 2.5 (T25/T40) (Tabulated UCS values can be found within Supplementary Table S2) A) UCS of all samples at T25. B) UCS of all samples at T40. C) Stress-strain profile of C LB S0-2.5 (T25) samples. D) Stress-strain of C LB S0-2.5 (T40) samples. E) Stress-strain profile of MT LB S0-2.5 (T25) samples. F) Stress-strain of MT LB S0-2.5 (T40) samples.

548 **Acknowledgments**

549 The authors gratefully thank Mark Foster and Kieran Nash for geotechnical support. This work
550 was supported by a Hossein Farny Scholarship from the University of Sheffield and the
551 Biotechnology and Biological Sciences Research Council (BB/P023703/1).

552

553 **Author Contributions**

554 S. J. A. S. S. S. and C. C. S. conceived the study, and designed the methodology. S. J. A
555 collected and analyzed the results. S. J. A wrote the manuscript with review from S. S. S. and
556 C. C. S. All authors read and reviewed the final manuscript.

557

558 **Competing Interests**

559 The authors declare no competing interests.

560

561 **Additional Information**

562 **Supplementary Information** The online version contains supplementary material available at:

563 **Correspondence** and requests for materials should be addressed to S. S. S. and C. C. S.

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