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Soil Improvement Using Microbial Induced Calcite Precipitation and Surfactant Induced Soil Strengthening

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SOIL IMPROVEMENT USING MICROBIAL INDUCED CALCITE PRECIPITATION AND
SURFACTANT INDUCED SOIL STRENGTHENING

By

MATTHEW P. DAVIES

A THESIS PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF NORTH FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE IN CIVIL ENGINEERING

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2018

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*To my wife and children
for their love and support through this adventure.*

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Abstract of Thesis Presented to the Graduate School
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SOIL IMPROVEMENT USING MICROBIAL INDUCED CALCITE PRECIPITATION AND
SURFACTANT INDUCED SOIL STRENGTHENING

By

Matthew P. Davies

December 2018

Chair: Raphael Crowley, PhD PE
Major: Civil Engineering

Microbially induced calcite precipitation (MICP) has been used for a number of years as a technique for the improvement of various geological materials. MICP has been used in a limited capacity in organic rich soils with varying degrees of success. Investigators hypothesized that microbially-induced cementation could be improved in organic soils by using a surfactant. Varying amounts of Sodium Dodecyl Sulfate (SDS) were added to soils of varying organic content and a mixing procedure was used to treat these soils via MICP. Treated specimens were tested for unconfined compressive strength (UCS). Results appeared to show direct relationships between SDS content and treated specimen strength although significant variability was present in the data. In addition, results also indicated that while addition of SDS during MICP treatment strengthens soil, the strengthening is likely from the formation of a calcium dodecyl sulfate (CDS) complex in which the CDS surrounds the soil in a matrix, and formation of MICP-induced calcite has very little to do with overall soil performance. As such, a new method for stabilizing loose soils dubbed ‘Surfactant-induced soil stabilization’ (SISS) was further explored by treating additional soil specimens. Samples treated using this technique showed increases in strength when compared to untreated specimens. In addition, preliminary data indicated that SISS treated specimens were

insoluble. The SISS technique presents a number of advantages when compared to traditional soil stabilization techniques. In particular it should be relatively low-cost and simple to administer since its only components are SDS and calcium chloride. Additionally, these constituents are relatively more sustainable than chemicals associated with more-traditional loose soil stabilization techniques.

CHAPTER 1 INTRODUCTION

1.1 Background Information

Stabilization of weak and compressible soils, such as clay and organic-rich soil, presents unique challenges in geotechnical engineering. Construction projects on such soils are prone to settlement and creep. These issues may be mitigated through various soil stabilization methods including excavation and replacement, surcharging, compaction, soil mixing, or grouting. Each of these methods has drawbacks. For large soil deposits, excavation/replacement is often cost prohibitive. Surcharging may be impractical for expedited construction, even with the use of wick drains. Soil mixing with cement may be prohibitively expensive because of the quantities of Portland cement associated with such treatments (Mullins and Gunaratne, 2015). As discussed by Mullins and Gunaratne (2015), in some cases a significant quantity of the grout or concrete acts as a void fill. Another drawback associated with soil mixing is that introduction of large quantities of Portland cement into the groundwater tends to significantly increase localized pH. This may be environmentally harmful. The use of lime has a long history in soil stabilization, typically with clayey soils. Soil mixing with lime induces a pozzolanic reaction that leads to stronger, stiffer, less-compressible soils. However, lime may also be environmentally harmful, and it may not be effective in all soil-types. Clay chemistry must be carefully assessed when lime treatment is recommended. Sulfate induced heaving may occur because of ettringite formation (Puppala et al. 2005). Fly ash has also been used as a chemical stabilizer and can also create pozzolanic reactions. It may contain trace amounts of arsenic, beryllium, boron, cadmium, chromium, dioxins, hexavalent chromium, cobalt, lead, manganese, mercury, molybdenum, selenium, strontium, thallium, and vanadium. Many of these components are environmentally harmful and/or carcinogenic. Ettringite formation is also a concern with fly ash and some clays.

Beyond these traditional techniques, several non-traditional soil treatment alternatives have been studied in recent years. Tingle and Santoni (2003) listed seven categories of such treatments, which include acids, enzymes, lignosulfonates, petroleum emulsions, polymers, salts, and tree resins. Blanck et al. (2014) assessed the effects of an acid solution, an enzyme solution, and a lignosulfonate on geotechnical properties of a low plasticity soil. More recently, microbially induced calcite precipitation (MICP) has gained traction as a potential sustainable, all-purpose soil stabilization method (DeJong et al., 2013 among others). MICP is typically considered a treatment for loose granular materials. Canakci et al. (2015) was able to show a reduction of compressibility and increase in angle of internal friction of a sandy organic silt (USCS classification OH) with approximately 60% organic material treated using MICP.

1.2 New Work Presented in this Thesis

This thesis presents work associated with two related studies whose overall goal was to strengthen various (primarily organic-rich) soils. The first study, documented in Chapter 2, was an attempt to use traditional MICP methodologies to treat with Florida organic-rich soils. The result of the study was little to no appreciable calcite formation and therefore minimal strength improvement. Then, sodium dodecyl sulfate (SDS) was added to the traditional MICP formula and the Florida organic-rich soils were treated again. Specimens with SDS exhibited significant strength improvement when compared to untreated specimens. However, further investigation showed that these strength improvements were most likely from a mechanism other than MICP.

The second study, documented in Chapter 3, was aimed at better-characterizing this new soil-strengthening mechanism. In particular, MICP ingredients were selectively and sequentially removed. Eventually, results showed that the observed increases in strength during the first study must have been due to a metal-ligand complex formation. This metal-ligand complex appears to have been formed in a non-aqueous stoichiometric environment that was the result of inverted

micellar formation whereby calcium (2+) ions reacted with the negatively charged head of the sulfate ion (-1) to form an ionic bond inside of the micelle holding it together. The tails of the inverted micelle pointing outward of the micellar structure were able to solubilize the organic content soils and further lock them into an immobile, impermeable matrix with increased strength properties.

1.3 Thesis Organization and Structure

Organization of this thesis is as follows:

- Chapter 2 presents results from the first, MICP-related study. The work in Chapter 2 was adapted and accepted for publication in the the proceedings of *Geo-Congress 2019*.
- Chapter 3 of this thesis presents results from the second study where the metal-ligand complex was further-explored. Some additional work will be required before these preliminary results can be fully explained.
- Chapter 4 presents a summary and conclusions from this study. In addition, recommendations for future work are presented as well.

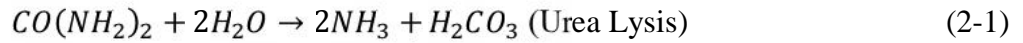
CHAPTER 2

MICROBIALY INDUCED CALCITE PRECIPITATION USING SURFACTANTS FOR THE IMPROVEMENT OF ORGANIC SOIL

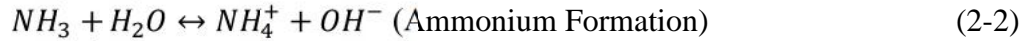
2.1 Background

2.1.1 Microbial Induced Calcite Precipitation Governing Reactions

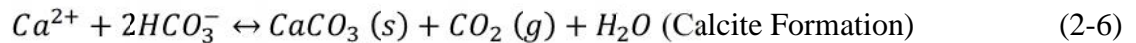
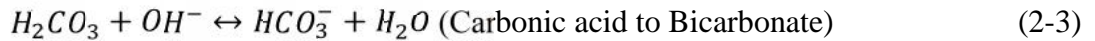
The microbial induced calcite precipitation (MICP) chemical reaction process has been detailed by several researchers including DeJong et al. (2006). To summarize, the reactions are initiated by the enzyme urease from *Sporosarcina pasteurii* which lyses urea into ammonia and carbonic acid as shown in Equation 2-1.



The ammonia reacts with water to form ammonium ions and hydroxide ions (Equation 2-2):



Ammonium is a weak acid and hydroxide is a strong base. As such, the pH of the system increases to an optimal value of approximately 9.5. Under these basic conditions, two moles of hydroxide ions react with the carbonic acid formed in the urea lysing step to generate a carbonate ion (Equation 2-3 and Equation 2-4), which then combines with dissolved calcium to form calcium carbonate (Equation 2-5). Calcium ions can also directly combine with bicarbonate ion to form calcium carbonate, carbon dioxide, and water (Equation 2-6).



The above reactions only occur in close proximity to the bacteria where the enzyme is released.

2.1.2 Treatment Techniques

Treating soil via MICP implies that *Sporosarcina pasteurii* (or another bacteria), urea, and calcium chloride must be introduced to the soil matrix. As discussed extensively by Mujah et al. (2016), introduction of these constituents may be accomplished via an injection method, a surface percolation method, or a premixing method. The injection method is probably the most-commonly studied method, and researchers have had significant success using it to treat soil in the past. Soil treated via this method have shown significant strength improvement. However, it does have its drawbacks as discussed by Mujah et al. (2016). In particular, non-uniform calcium carbonate cementation may develop as a result of pore clogging. These heterogeneous calcium carbonate distributions lead to variations in both strength and hydraulic conductivity. Researchers have attempted to address these issues by varying injection rates or treating via micro-dosing whereby bacteria and/or feed stock (i.e. calcium chloride and urea) are intermittently introduced to the soil. Research aimed at enhancing this method is ongoing, and ultimately this may become the preferred treatment method in the field.

The surface treatment technique has been proven to be useful in terms of generating relatively homogeneous specimens. However, as discussed by Mujah et al. (2016), it has its limitations as well. In particular, it may not be useful for fine-grained soils, and there is some practical limitation in terms of the depth to which surface-introduced constituents can permeate.

As discussed by Mujah et al. (2016) the premixing method leads to very homogenous specimens and may be achieved two ways. The first method involves mixing bacteria, urea, and calcium chloride together until homogeneity is achieved. Then, the specimens are allowed to cure. Yasuhara et al. (2012) and Zhao et al. (2014a) reported significant increases in unconfined compressive strength (UCS) when compared with untreated specimens using such a method. Zhao

et al. (2014b) reported a premixing method whereby bacteria/sand were submerged in a calcium chloride/urea bath.

2.1.3 Goals and Objectives

The goal of this study was to assess the applicability of the mixing method/MICP as a treatment technique for soil with significant organic content. As discussed in Chapter 1, Organic-rich soils are particularly troublesome when they are present below roadways and other constructed facilities as they are susceptible to settlement and creep with will impact both the serviceability and ultimate limit states. Ultimately, the goal was to develop an in-situ treatment technique for organic-rich soil via MICP.

2.2 Initial Treatment Methodology

As discussed in Chapter 1, current soil improvement techniques for organic-rich soils in Florida include preloading, cutting and replacing, and grout mixing. Grout mixing is the most effective of these techniques, but it requires significant quantities of Portland cement, increases the unit weight of the soil leading to additional consolidation, has a significant carbon footprint, and may pose environmental issues from leaching. In the context of replacing grout mixing with a more sustainable technology such as MICP, soil mixing techniques such as those discussed by Mujah et al. (2016), may be suitable. Additionally, in terms of assessing “suitability,” research indicated that creating more-uniform specimens using a simple technique would yield quicker, more-uniform results. Therefore, a mixing technique was used throughout this study. Specifics of the method were as follows:

- Soil with an initial organic content of approximately 50% was obtained from a natural soil deposit near SR-33 in Polk County, FL. This material was dried, homogenized, and sieved.
- 50/70 Ottawa sand (quartz) was added to the organic soil to yield three soil batches with organic contents of 10%, 30%, and 50% by weight

- The soil was pluviated into 50.8 mm by 101.6 mm cylinder molds until the molds were approximately 75% full.
- *Sporosarcina pasteurii* NRS929 was obtained from the USDA. Bacterial cultures were grown at 30C with aeration by shaking in Brain Heart Infusion broth supplemented with 2% urea. Cultures were grown to an optical density (OD) greater than 2.0 for all experiments. 40 ml of the solution was added to the soil and hand mixed using a spatula.
- 80 ml of a 2.5M urea/2.5M calcium chloride solution was added to each soil/bacterial mixture (40 ml of urea/40 ml of calcium chloride). The urea/calcium chloride/bacteria/soil was hand-mixed using a spatula.
- The specimens were allowed to air cure for a minimum for 48 hours.
- After curing, the molds were opened using a Dremel® tool and the specimens were extracted.

Interestingly, the above technique did not produce significant calcification or cementation of the 50% organic content specimens and minimal calcification for both the 10% organic content and 30% organic content specimens (Figure 2-1(a)). The above technique was repeated using 50/70 Ottawa sand, and significant calcification was observed. Ottawa 50/70 specimen cementation appeared to be nearly homogeneous (Figure 2-1(b)).

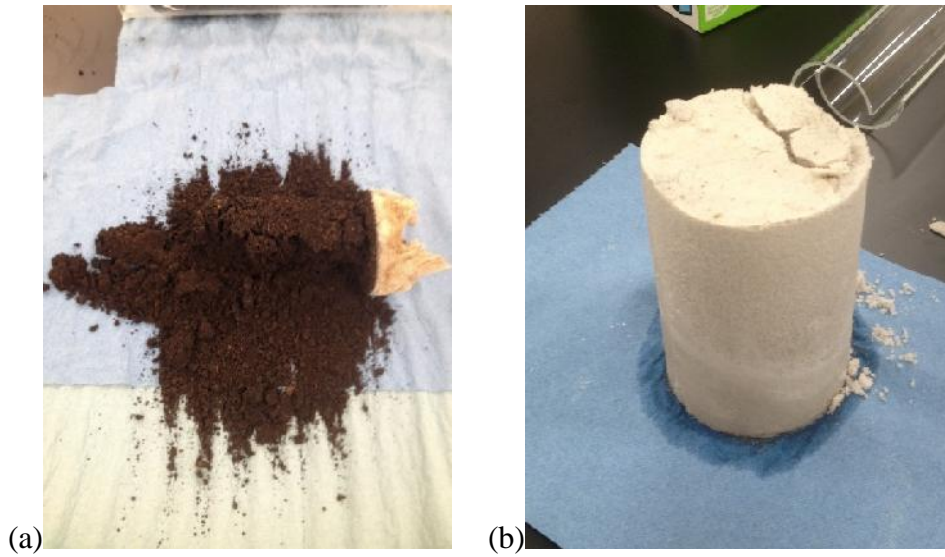


Figure 2-1. (a) 50% Organic Content Soil after MICP treatment (b) Example of fully-cemented 50/70 Ottawa sand specimen after MICP treatment

Investigators were aware that other researchers had achieved some success in cementing organic-rich soil – Inagaki et al. (2011) and Canakci et al. (2015) – which made results even more troublesome. These results were puzzling, but holistically indicated that there must be an inherent difference between Ottawa sand and these organic-rich soils. Investigators hypothesized that the reason the procedure worked well in sand and poorly in these organic-rich soils may be due to surface charge differences between quartz sand and organic particles.

2.3 Soil Particle Geochemistry and the Need for a Surfactant

In general, Florida organic-rich soils are created from the residues of decomposition of living matter (plant, animal, and microbial). Water-soluble compounds tend to be leached, leaving behind relatively aliphatic organic compounds such as carbohydrates, fats, lignins, and proteins. As decomposition occurs, aliphatic organics are broken down into simple water insoluble compounds that tend to be non-polar and, therefore, hydrophobic (Figure 2-2(a)). On the other hand, much like water molecules, quartz sand tends to be polar (Figure 2-2(b)). While the structure of quartz (Figure 2-2b) does not strictly have a negative charge, the surface has a partial negative

charge resulting from the dipole created by the uneven distribution of electron density around the oxygen atoms.

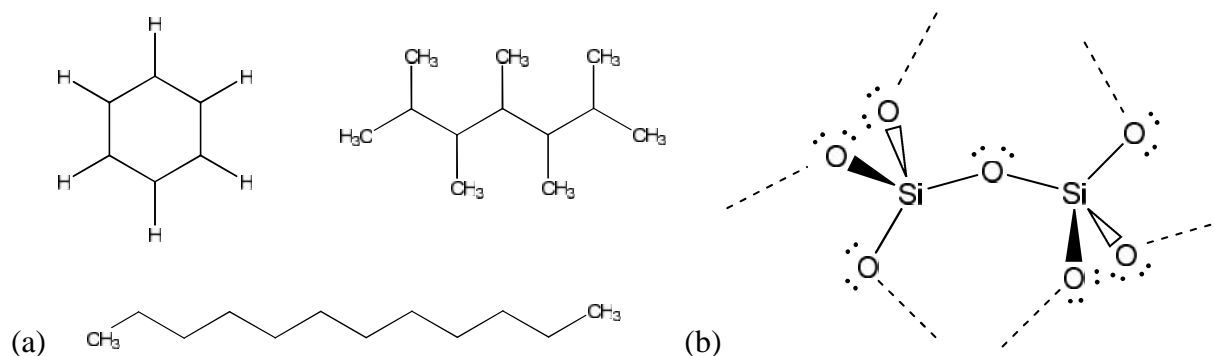


Figure 2-2. (a) Typical molecular structure of aliphatic organic compounds; top-right is cyclohexane; top-left is 2,3,4,5,6-methylheptane; bottom is decane; (b) Molecular structure of quartz sand

As discussed by DeJong et al. (2010), calcium carbonate produced by bacterial ureolysis tends to fill the interstitial spaces between soil particles and bacterial cells. *Sporosarcina pasteurii* has a negative surface charge, and as discussed above, quartz sand has a polar dipole. Anecdotal evidence of the charged particle hypothesis was found when specimen MICP treatments were conducted in different specimen molds. It was noted that during quartz sand treatments, carbonate cemented specimens tended to adhere to negatively-charged surfaces such as glass and aluminum. However, when MICP was induced on specimens touching neutrally-charged surfaces such as plastics, the carbonate cemented specimens did not adhere to these surfaces. Altogether, this led investigators to believe that surface charges may play a role in MICP calcification, and that neutrally-charged organic-rich soil did not adhere to the calcium carbonate minerals that were being formed during ureolysis.

In an attempt to overcome this issue, investigators sought to induce a treatment that would mimic the polar dipole surface of quartz sand. It was hypothesized that addition of an anionic

surfactant might be employed. Sodium Dodecyl Sulfate (SDS; Figure 2-3) contains a linear twelve-carbon chain tail and a negatively charged polar sulfate head.

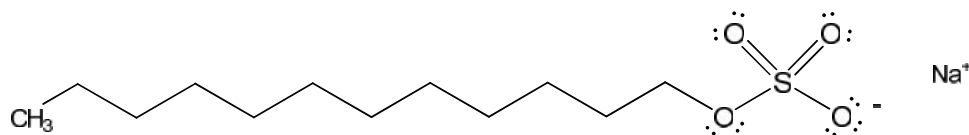


Figure 2-3. Sodium Dodecyl Sulfate (SDS)

When dissolved in an aqueous solution, the sodium ion disassociates from the polar sulfate head/carbon tail and the sulfate heads align with one another creating spherical micelles (Figure 2-4). It was hoped, that when added to soil, the SDS micelles would surround the organic matter particles, thereby creating a mimicked surface on which the calcium carbonate ions could adhere. Several specimens of organic-rich soil were mixed with SDS in various percentages using a spatula. The MICP mixing procedure described above was repeated using the SDS-organic-rich specimens. Then, UCS tests were conducted on the treated specimens (ASTM D2166).

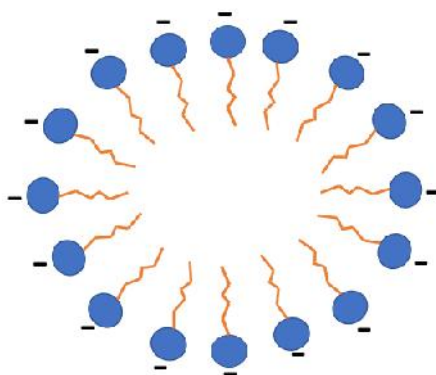


Figure 2-4. SDS Micelle Schematic

2.4 Results and Discussion

Initial results were very positive and initially confirmed investigators' hypotheses in that adding SDS produced soil columns that appeared to be fully or nearly fully homogeneously calcified (Figure 2-5).

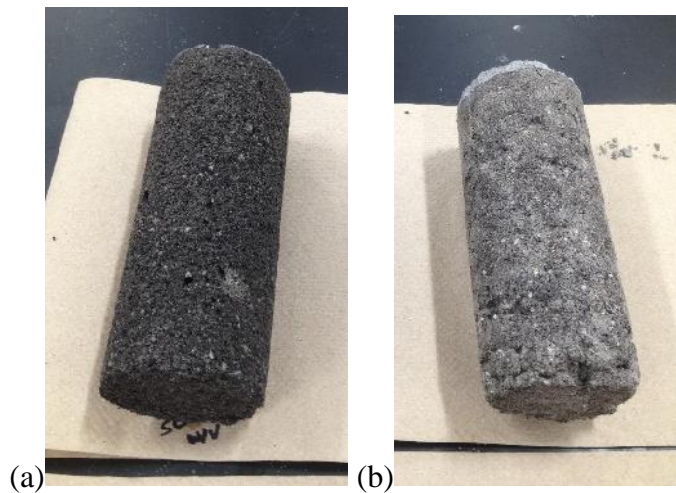


Figure 2-5. SDS-Organic-Rich Specimens after MICP Treatment Showing (a) Soil with 50% Organic Content by Weight Mixed with 50% SDS by Weight; and (b) Soil with 50% Organic Content by Weight Mixed with 80% SDS by Weight

Relationships were developed between SDS quantity and UCS (Figure 2-6) although significant scatter was observed in the data. Further investigation showed that these apparent strength increases were not the result of MICP, but rather a different mechanism. After the initial round of UCS tests were completed, additional specimens were prepared. The first set of specimens consisted of organic soil, SDS, and calcium chloride solution only (i.e. no microbes nor urea). The second set consisted of organic soil, SDS, calcium chloride, and urea solution (still no microbes). Three SDS percentages (by weight) were mixed – 30%, 60%, and 90%. After treatment, these specimens were all subjected to UCS testing. Results (Figure 2-6) showed that the specimens treated without microbes were the strongest for low SDS percentages. At higher SDS percentages, strengths without microbes were similar to strengths from MICP treatment.

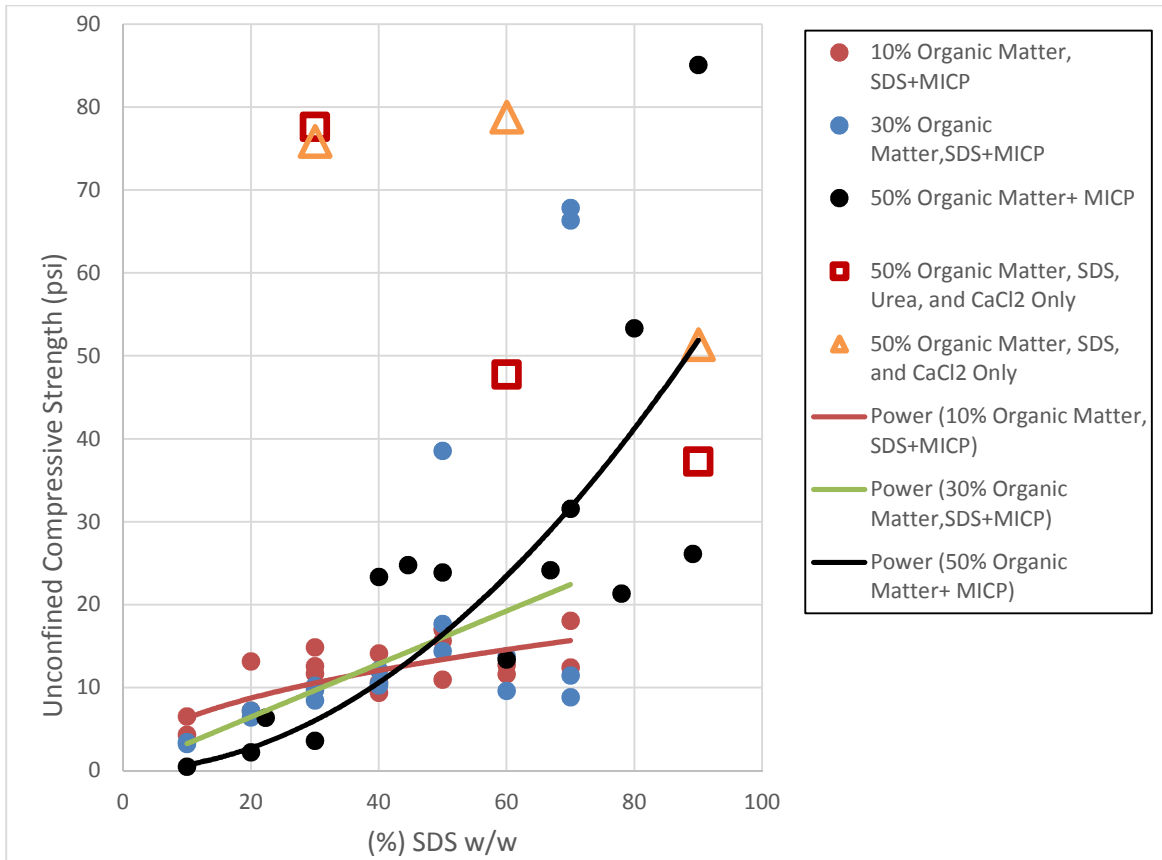


Figure 2-6. UCS versus % SDS By Weight for MICP treated Organic-Rich Soil

This treatment procedure was repeated, and a new round of MICP-treated specimens were prepared. These samples were subjected to dissolution testing after curing whereby they were submerged for 48 hours. Results are shown in Figure 2-7 for soil with an initial organic content of 100% by weight.

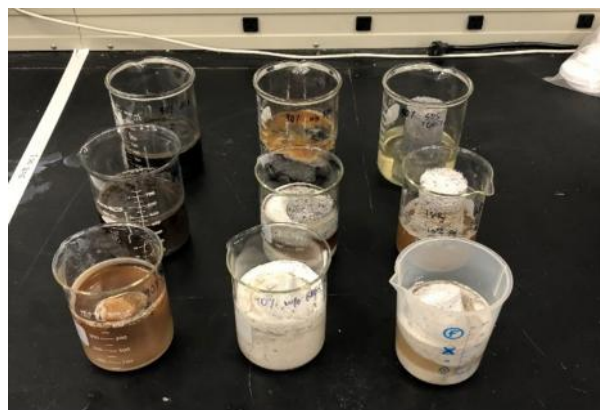


Figure 2-7. Dissolution Testing Results after 48 Hours

The left-hand column in Figure 2-7 shows MICP-treated specimens using SDS, urea, calcium chloride and microbes. The middle column shows specimens treated using SDS, urea, and calcium chloride only (i.e. microbes omitted). The right-hand column shows specimens treated with SDS and calcium chloride only (i.e. both microbes and urea omitted). In Figure 2-7, the top row are specimens that were mixed with 30% SDS by weight; the middle row are specimens that were mixed with 60% SDS by weight; and the bottom row are specimens that were mixed with 90% SDS by weight. As shown, for a given SDS percentage, the specimens treated with calcium chloride and SDS only tended to dissolve less than specimens where urea was included. And, the specimens treated using microbes appeared to be the most dissolvable.

These results suggested that the combination of SDS and calcium chloride was likely responsible for the apparent strengthening and that including microbes and/or urea inhibited that strengthening mechanism to some extent. Scanning electron microscope and energy dispersive spectroscopy (SEM-EDS) analyses were conducted on specimens treated both with and without microbes/urea. In all cases very little calcium carbonate was observed. However, sodium chloride deposits were suggested by SEM-EDS analyses (Figure 2-8).

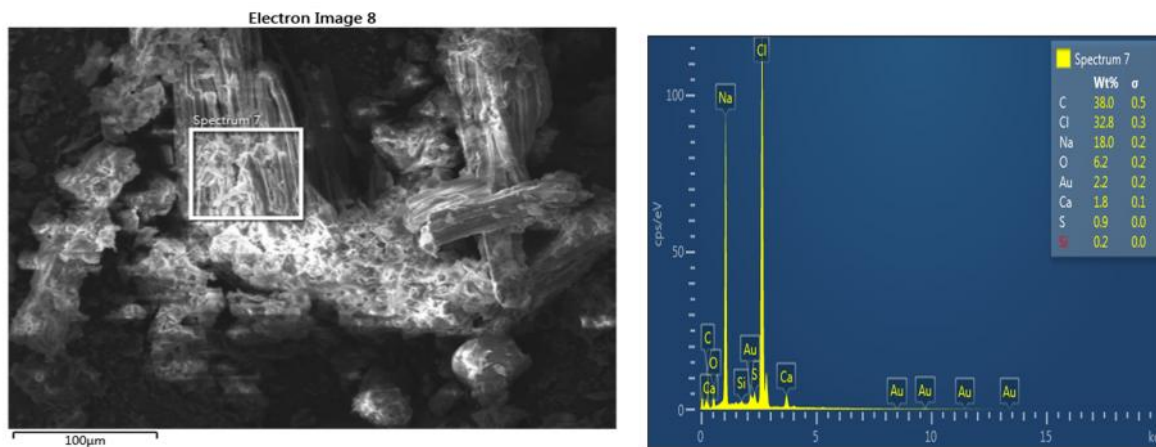


Figure 2-8. SEM/XRD Results from Specimen Treated with CaCl_2 and 30% SDS Only Showing Apparent NaCl Crystals

Sodium chloride is highly dissolvable and results from dissolution testing indicated that resulting organic specimens treated with 30% SDS and calcium chloride were relatively insoluble. Therefore, it would appear that the specimen strengthening must have been the result of a mechanism that was neither sodium chloride nor calcium carbonate crystallization. Investigators believe the strengthening was due to a combination of positive calcium (+2) ions and the negatively charged (-1) sulfate head/carbon tail portion of the SDS in that the calcium ions formed metal-ligand complexes and created a matrix of micelles that held the soil together (Figure 2-9). This metal-ligand complex may be better-characterized as a calcium-dodecyl sulfate (CDS) complex and has been dubbed surfactant-induced soil stabilization (SISS).

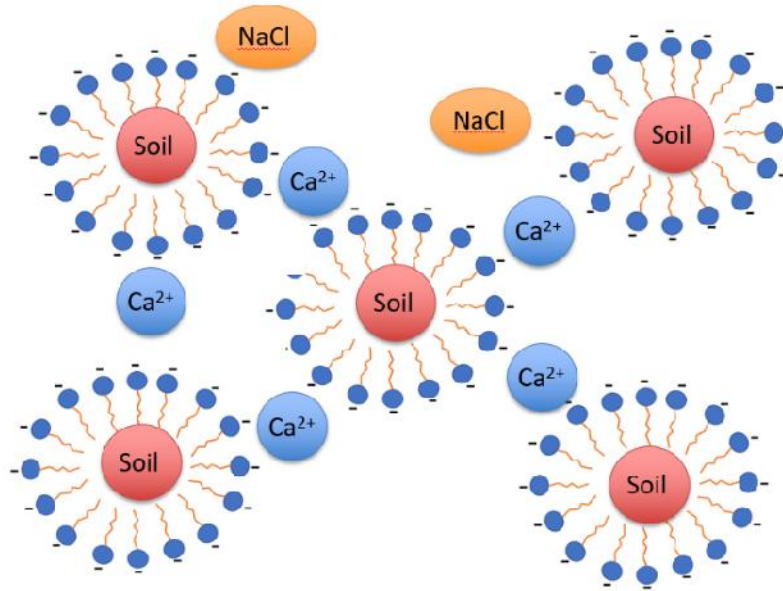


Figure 2-9. Possible Explanation for Apparent Strengthening from SDS- CaCl_2

When microbes were included, fewer calcium ions were available to form this matrix because of the calcium carbonate reaction described by Equations 5 and 6. Inclusion of urea also

produced weaker/more dissolvable specimens. This may indicate that the urea denatured the organic soil particles, similar to its behavior with proteins. Initially, it was thought that a possible macroscopic structure for the metal complexing soil matrix might be that of Figure 2-9 where the organic soil is solubilized into the interior of the micelle, and calcium ions ionically bond to the exterior negative charge of the polar sulfate heads.

CHAPTER 3

SURFACTANT-INDUCED SOIL STABILIZATION (SISS): A NEW TECHNIQUE FOR LOOSE SOIL STABILIZATION

3.1 Genesis of Soil-Surfactant Treatment

As discussed in Chapter 2, SDS is a common anionic surfactant with both polar and non-polar surface properties. It was hypothesized that the SDS would both solubilize the organic material and provide a negatively charged surface on which the bacteria could calcify. Recall, from Chapter 2, that SDS consists of a sodium-sulfate head bonded to a twelve-carbon chain tail. In aqueous solution, the sodium ion disassociates from the dodecyl sulfate portion of the SDS molecule yielding a polar hydrophilic head and a neutrally-charged hydrophobic tail. When the concentration of any surfactant passes its critical micelle concentration (CMC), the hydrophilic heads and the hydrophobic tails tend to align with one another creating micelles (Figure 3-1(a)). As discussed by Zapf (2002), micelle shape may vary depending on interfacial conditions. Common micelle shapes include bilayers, spheres, rod-like structures, disc-like structures, vesicles, lamellae, and a sponge-phase. Regardless of the shape of the micelle, they tend to interact similarly with neutrally-charged particles in aqueous solutions. When in solution, micelle formation results in interior hydrophobic pockets that can absorb neutrally-charged particles coupled with hydrophilic exteriors capable of interacting with water or other polar solvents.

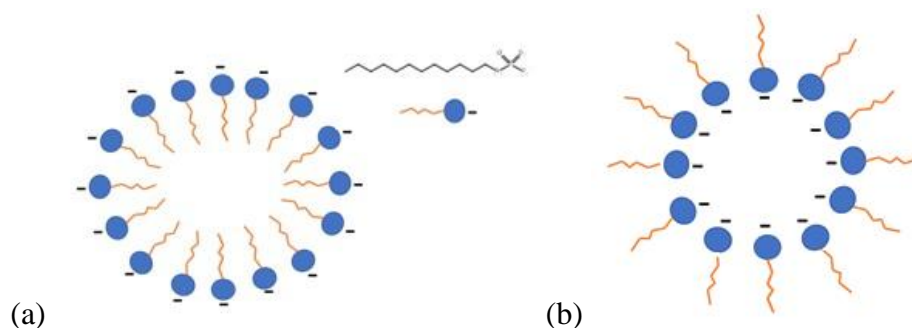


Figure 3-1. (a) SDS Micelle Structure in Aqueous Solution, (b) SDS Micelle Structure in Non-Aqueous (Hydrophobic) Solution

In this way, organics can absorb into the interior of the micelle and effectively be solubilized into an aqueous media. In hydrophobic solutions (liquid oils), or mixed hydrophobic/hydrophilic solutions, where the mixed solution is far more hydrophobic than hydrophilic, inverted micelles also occur with an interior hydrophilic pocket containing the polar “heads” and a non-polar exterior where the hydrophobic “tails” point outward (Figure 3-1(b)). This occurs to reduce the overall system entropy in hydrophobic media and to align “like” chemical properties. As discussed in Chapter 2, the reason SDS was added to the MICP treatment formula was that investigators hypothesized that the SDS may both solubilize the organic material and provide a negatively charged surface on which the bacteria could calcify.

3.2 Sumamry of Previous Applicable Testing/Results

The following is a summary of applicable new testing presented in the previous chapter:

- Several SDS-MICP treated specimens were prepared and subjected to UCS testing. Preliminary results showed a direct relationship between the quantity of SDS and compressive strength. These results were presented in Figure 2-6.
- After these preliminary tests, investigators conducted another series of tests in an attempt to verify that microbially-induced calcite (as opposed to another mechanism) caused the observed strength increases. Specifically, specimens were prepared where constituents

associated with the SDS-MICP were sequentially omitted such that soil was treated with the following Formulas:

- a) Soil with 50% organic content, SDS, and deionized water only,
- b) Soil with 50% organic content, SDS and 2.5 M calcium chloride only, or
- c) Soil with 50% organic content, SDS, 2.5 M calcium chloride, and urea only, or
- d) Soil with 50% organic content, SDS, 2.5 M calcium chloride, urea, and *Sporosarcina pasteurii* (i.e. all constituents required for MICP).

These specimens were also subjected to UCS and added to Figure 2-6. A summary of these results is presented below in Table 3-1:

Table 3-1. Strengths of Organic Formulas

<u>Formula</u>	<u>SDS (% by mass)</u>	<u>UCS (psi)</u>
a	30	N/A
	60	N/A
	90	N/A
bb	30	11.0
	60	11.4
	90	7.4
c	30	11.1
	60	6.9
	90	5.4
d	30	2.5
	60	0.9
	90	1.4

- As shown, specimens treated using Formula a showed no strength improvement. Specimens treated using Formula c and Formula d showed some UCS improvement. However, investigators were surprised to learn that specimens treated using Formula d performed the best during UCS testing.

- Investigators also performed a series of dissolution tests on various specimens treated using Formula a through Formula d. The dissolution tests consisted of submerging specimens for a minimum of 24 hours. Specimens treated using Formula c and Formula d were both highly dissolvable while specimens treated using Formula b were insoluble. This was also surprising since the end-product of MICP treatment, calcium carbonate, is insoluble. Thus, another mechanism must have been responsible for the apparent strength increases. This new mechanism was hypothesized to be the result of a CDS complex formation that has been dubbed SISS.

3.2 New Treatments

To further explore and generalize these unanticipated results/better characterize SISS-treated soil properties, additional specimens were prepared using Formula (b). Four different soil types were tested: soil with 50% organic content mixed with Ottawa 50/70 sand to yield soil with 30% organic content (organic soil); Ottawa 50/70 sand (Ottawa), Tennessee ball clay (TBC), and brown clay (Clay1). Soil properties associated with TBC and Clay 1 are presented below in Table 3-2:

Table 3-2. Properties of Clay Materials

Clay	Tennessee Ball Clay (TBC)	Brown Clay (Clay 1)
Liquid Limit	57.9	30.4
Plastic Limit	26.2	22.9
Plasticity Index	31.7	7.5
USCS Classification	CH	CL
Percent Clay	80%	65%

Powdered SDS was added to the dry soils at 30%, 50%, and 60% by mass and the soil-SDS was mixed using a spatula. Then, 40 ml of 2.5 M calcium chloride solution was added to these soil-SDS mixture. The slurry was poured into 5.08-cm by 10.16-cm plastic cylinder molds and allowed to air dry for a minimum of 2 hours. Although this 2-hour curing window was used, investigators observed noticeable specimen hardening within 20 minutes. After curing, the molds were cut using a Dremel® tool and the specimens were extracted. The specimens were then oven

dried at 60°C for 24 hrs. Initial results were very promising in that all treated specimens appeared to be strongly cemented (Figure 3-2).



Figure 3-2. Cemented specimens of 100%, & 30% SDS, CaCl_2 , organic content soil specimens respectively

After curing, UCS testing was conducted on treated specimens. In addition, these specimens were internally inspected after testing. Finally, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were conducted on portions of select treated specimens.

3.3 Results and Discussion

Results from UCS testing on organic soil, Tennessee ball clay (TBC), brown clay (Clay 1), and Ottawa sand is presented below in Figure 3-3:

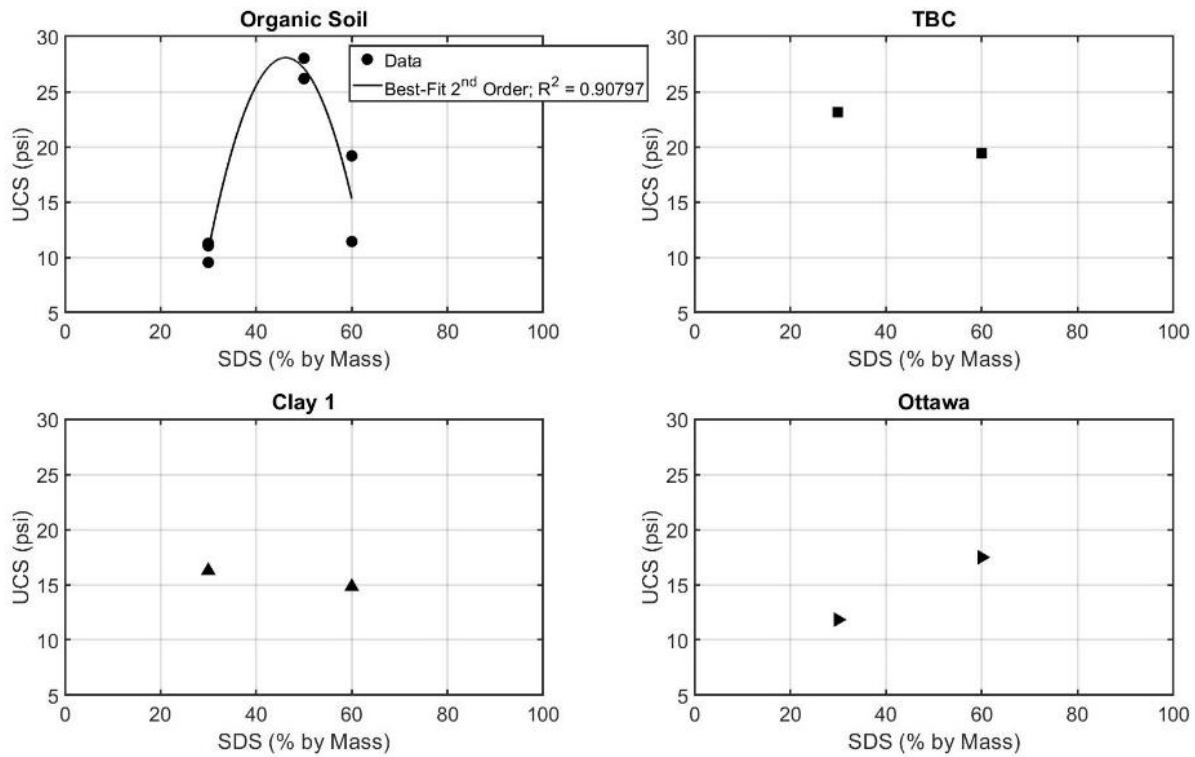


Figure 3-3. UCS versus Percent SDS by Mass for SDS and CaCl₂-Treated Soils

3.3.1 Results in Organic Soil

As shown above, UCS results showed an apparent strength maximum near the 50% SDS ratio. This apparent maximum is attributed to a hydrophobic balance between the ratio of organic soil to SDS. In other words, the hydrophobic tails of the SDS molecules appeared to solubilize the hydrophobic portions of the organic soil. At low concentrations of SDS, hydrophobicity appears to be insufficient to stabilize the available organic content soil. In other words, at low concentrations of SDS, all of the SDS has reacted to form the CDS complex and there was an excess of unreacted calcium chloride in the matrix. Likewise, at high concentrations of SDS, all of the organic content soil has been stabilized and the decrease in strength is due to the high concentrations of non-soil stabilized unreacted SDS. A photograph of the treated organic soil is presented below in Figure 3-4:

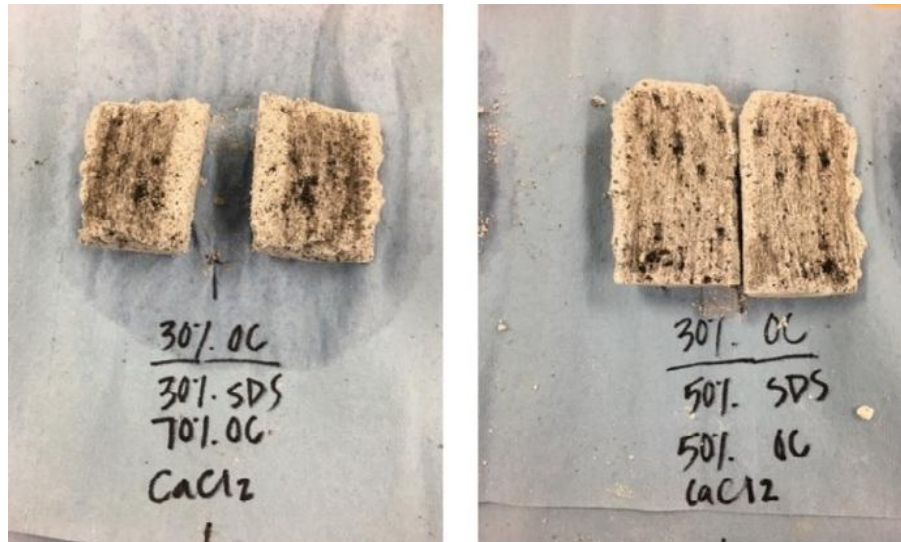


Figure 3-4. Internal inspection of UCS tested Organic Content Specimens

Internal inspection of this 30% organic content specimen showed slight inconsistencies in the distribution of the larger-sized soil particles within the CDS matrix, whereas the smaller sized soil particles seem to be relatively homogeneously distributed. It is believed that some of the scatter in the data is due to this inhomogeneity. As such, future treatments should use organic soil sieved to 200mm-300mm.

3.3.2 Results for Other Soil-Types

As shown in Figure 3-3, strength appeared to be inversely related to SDS concentration for both clay specimens. The Ottawa specimens however, show increases in strength with increasing SDS concentration. These behaviors are believed to be due to the particle size of the respective soils. Ottawa sand tends to contain larger void spaces than clays. It would appear that the SDS micelles better fit into the larger sand voids than the relatively smaller voids in the clay matrices. Further, as the clay particle sizes are much smaller than either the Ottawa or the organics, Van der Waals forces may also play a role in CDS complex formation. This could explain the decrease in strength of both clays as SDS concentrations increase. However, it is also possible that optimum strength as a function of SDS occurs at a lower (i.e. less than 25%) SDS quantity. These issues

need to be further-explored in future research. Photographs of treated inorganic soil specimens are presented below in Figure 3-5. As shown, soil particles appear to be approximately evenly distributed in each of these specimens.

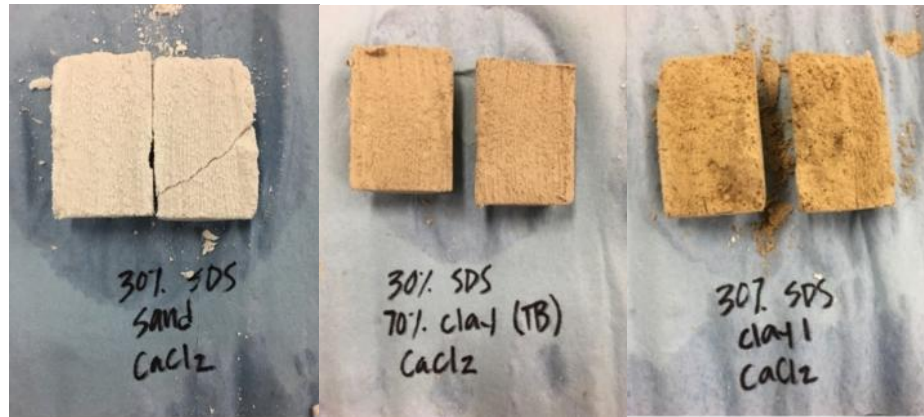


Figure 3-5. Internal inspection of UCS tested Ottawa, TBC, and C1 Specimens

3.3.3 SEM-EDS Results

Select SEM-EDS results are presented in Figure 3-6.

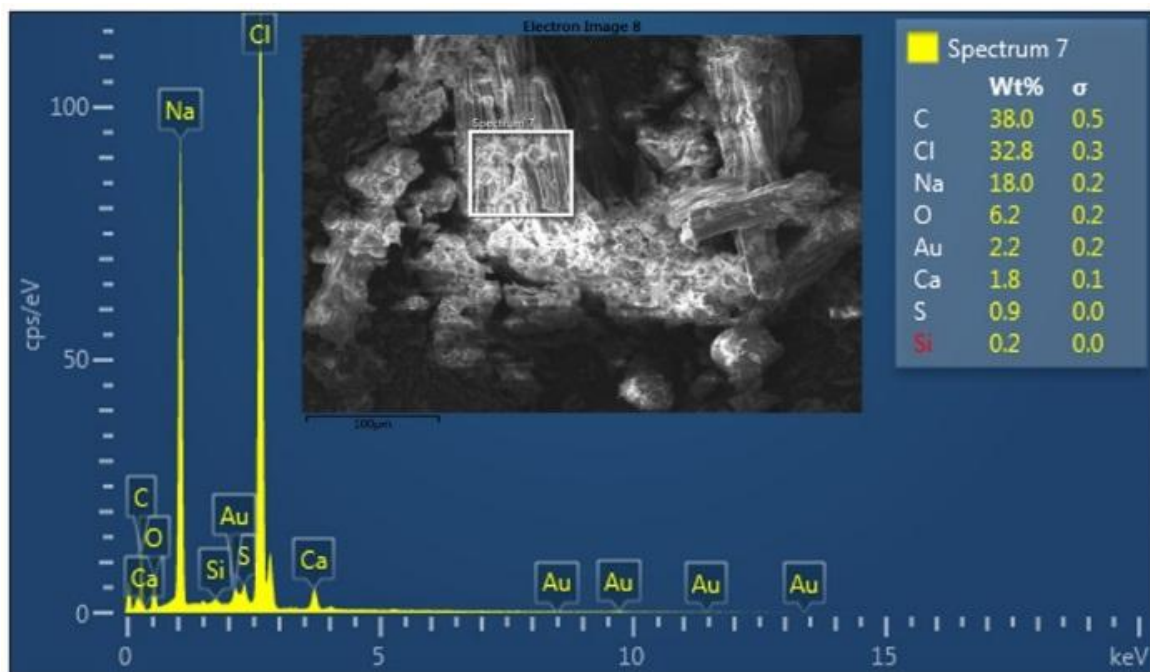


Figure 3-6. SEM/EDS Results of 30% SDS, CaCl₂, and organic soil specimen showing apparent NaCl crystals

As shown, sodium chloride deposits are suggested by this image and EDS data that show high concentrations of both sodium and chlorine. However, sodium chloride is highly dissolvable and as discussed above, soil specimens treated with SDS and calcium chloride are insoluble. This suggested that the specimen strengthening was not simply precipitation of sodium chloride. In other words, if the specimens had been dissolvable, one could have argued that the observed results were caused by precipitation of sodium chloride (i.e. sodium from the SDS combining with chlorine from the calcium chloride). Therefore, a more-likely explanation for the observed results is that each positively-charged calcium ion bonded with two of the negatively-charged dodecyl sulfate) ions as shown in Equation 7 and Figure 3-7.

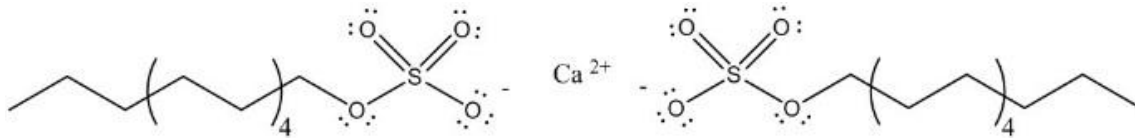
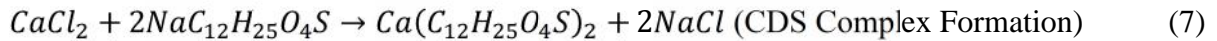


Figure 3-7. Calcium Dodecyl Sulfate Complex

Macroscopically, a multitude of these CDS complexes appear to form inverted micelles above the CMC in a substantially hydrophobic environment. This leads to a secondary matrix of micelles from the combination of positive calcium (+2) ions and the negatively charged (-1) sulfate head/carbon tail portion of the SDS (Figure 3-8). As discussed above, this CDS complex appears to be strong enough to bind soil particles together.

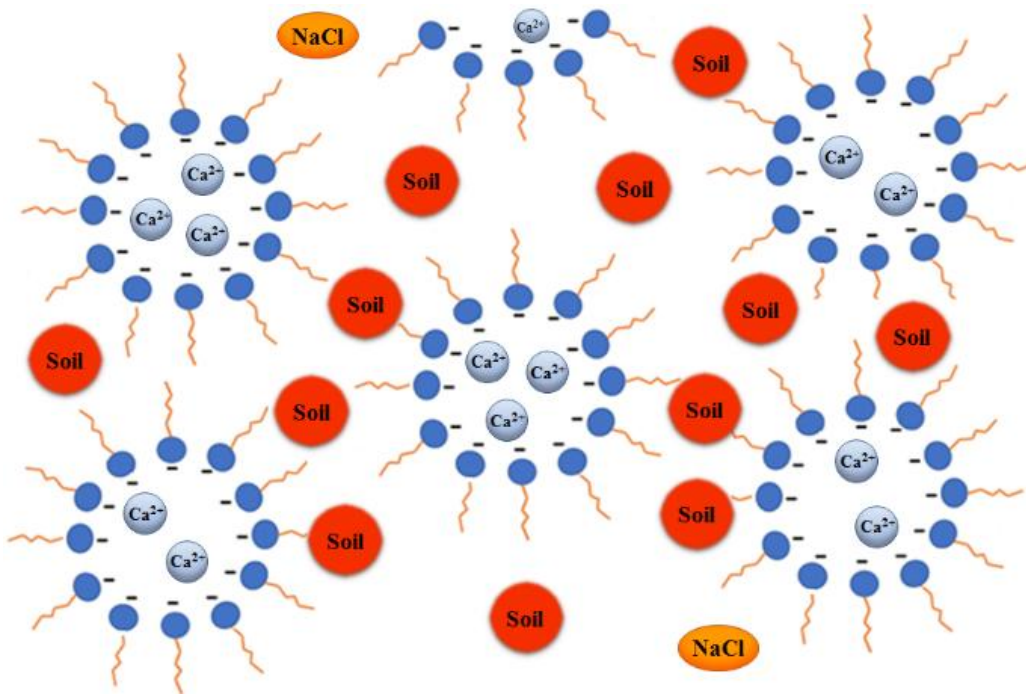


Figure 3-8. Possible Explanation for Apparent strengthening from SDS- CaCl_2 complex

The formation of the CDS complex prevents the micelle from achieving a hydrophilic exterior as the hydrophilic heads of the micelles are ionically bonded to Ca^{2+} ions. This is likely the reason that treated soil strength increased and that treated specimens were insoluble. Put another way, SEM-EDS results appeared to support the hypothesized formation of the CDS complex discussed above with one exception – in Chapter 2, the micelles were assumed to point outward. However, data from this chapter appears to show that the micelles are inverted.

CHAPTER 4

SUMMARY, CONCLUSIONS, AND FUTURE WORK

- MICP was used to treat organic-rich soil specimens from Polk County, FL using a mixing procedure. Results showed that MICP was ineffective for these soils, and treatment produced loose specimens that behaved similarly to untreated specimens. The procedure was repeated in quartz sands and relatively homogeneously strengthened specimens were produced. Others have had some success using MICP in organic soils. However, results showed that the soil from Polk County, FL responded poorly to a mixing treatment method. It is possible that this soil may respond better to MICP treatment using microdosing. Or, the soil from Polk County may be unsuitable for MICP treatment.
- Investigators hypothesized that MICP treatment could be improved using by adding a surfactant to the MICP formula. Results showed the soil was strengthened, but likely via a different mechanism – the creation of a calcium dodecyl sulfate (CDS) complex in which the CDS precipitate formed a micellar matrix around the soil particles thereby locking them into place and increasing strength properties.
- To better understand these results, a series of tests were conducted using various soil types and SDS percentages. Results confirmed previous preliminary testing in the sense that the CDS complex appears to consistently stabilize loose/weak soil, is very hard, insoluble in pure water, and very strong. However, results also showed that this CDS complex is likely the result of inverted micelles.
- This new method for soil improvement has been dubbed the Surfactant-induced soil strengthening (SISS) technique and may be an attractive new method for soil strengthening that could be used in the future to stabilize organic soil.
- While the CISS technique stabilized and increased the strength of organic-rich soil and Ottawa sand, it did not lead to an increase in strength in silt and/or clay soils. These latter results require further investigation.

- Overall, the SISS technique may be an attractive new method for soil strengthening and coalescing of loose soils into a new conglomerate that could potentially stabilize foundations on organic-rich and other weak soils.
- Discovery of the new SISS treatment technique is the most significant outcome from this work, and ultimately, SISS may supplant MICP as the environmentally-friendly, all-purpose loose soil treatment technique. However, investigators have not completely abandoned MICP treatment in organic-rich soils either. Tests are underway to utilize magnesium chloride and strontium chloride solutions with SDS in an attempt to create a SISS strengthening matrix similar to the one found during this study while leaving sufficient calcium ions present to form calcium carbonate. In other words, eventually it may be possible to develop a hybrid SISS-MICP treatment that combines the best aspects from both these techniques that results in even stronger soil specimen.
- The SISS treatment technique is a new technology. As such, significant future work will be required. The next steps should include optimization of the reaction stoichiometry. In addition, other geotechnical properties (beyond UCS) should be characterized in treated specimens – especially shear stress and compressibility.
- In the future, it may also be useful to explore using other of other anionic surfactants during SISS treatment other than SDS. It is possible that these other surfactants may possibly affect micellar shape and solubility properties positively. Ultimately, this may lead to even stronger specimens.

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APPENDIX A SEM IMAGES FOR SDS/ORGANIC CONTENT SPECIMENS

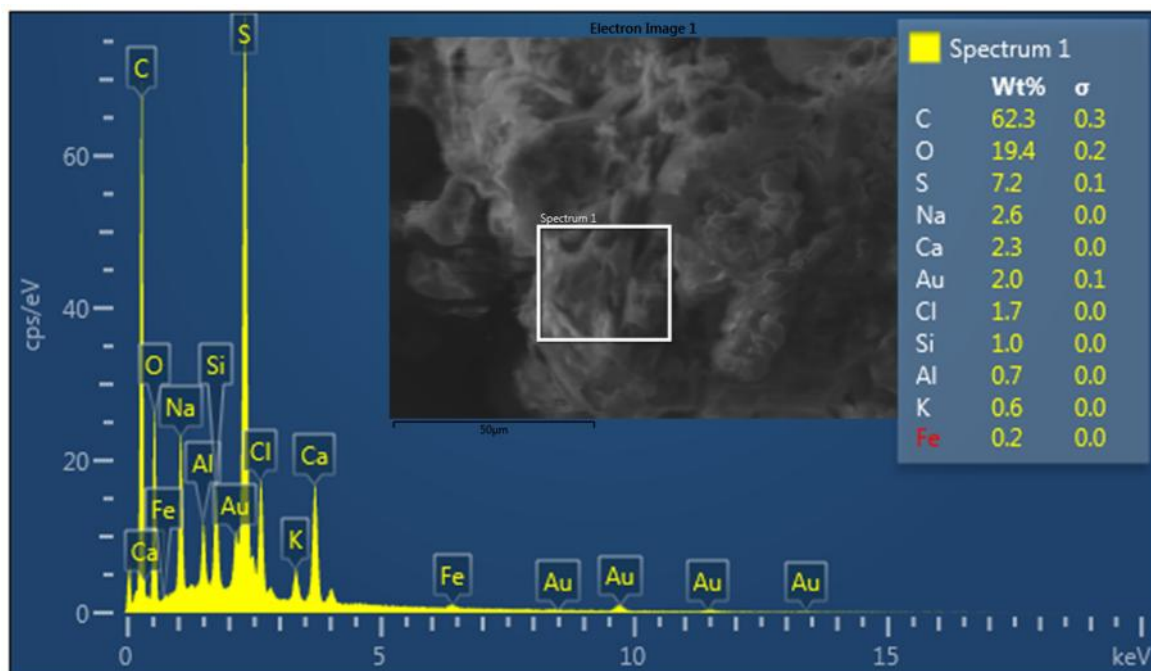


Figure A-1. SEM/EDS 30% Organic content, *Sporosarcina pasteurii*, CaCl_2 , Urea, & 30% SDS Site 1

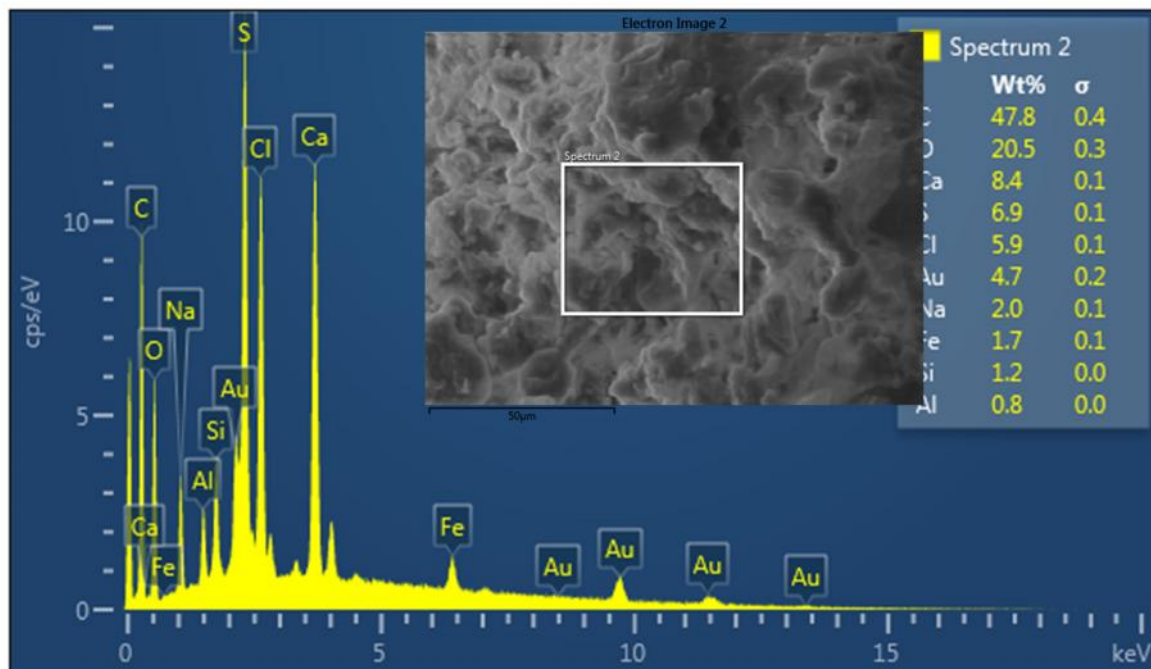


Figure A-2. SEM/EDS 30% Organic content, *Sporosarcina pasteurii*, CaCl_2 , Urea, & 30% SDS - Site 2

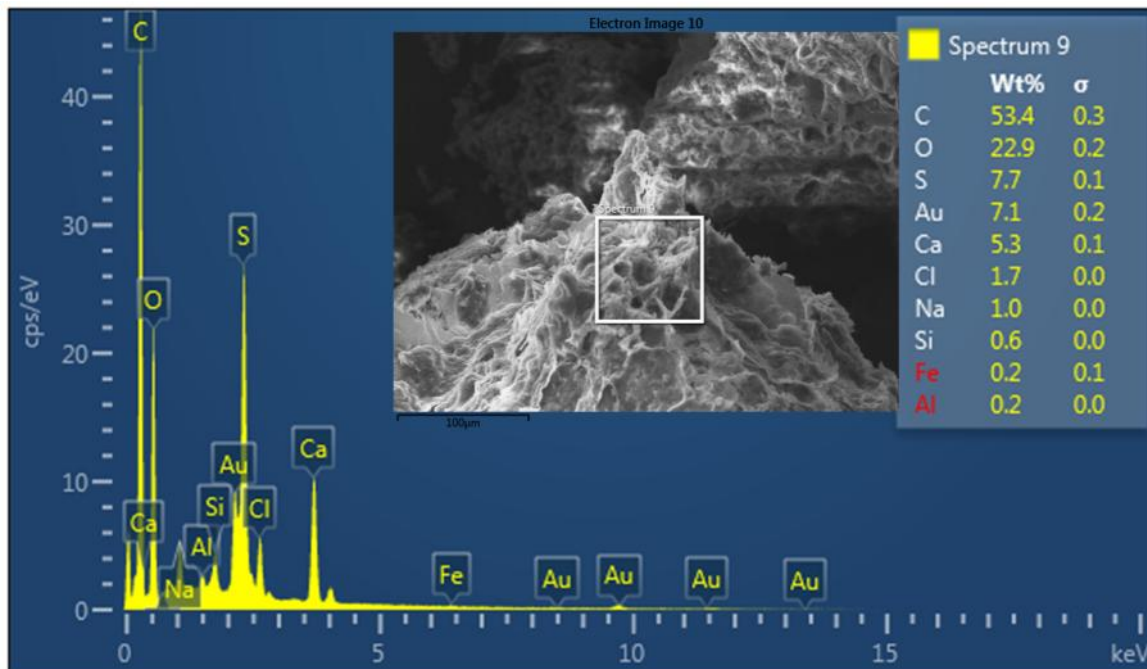


Figure A-3. SEM/EDS 30% Organic content, CaCl_2 , Urea, & 30% SDS – Site 1

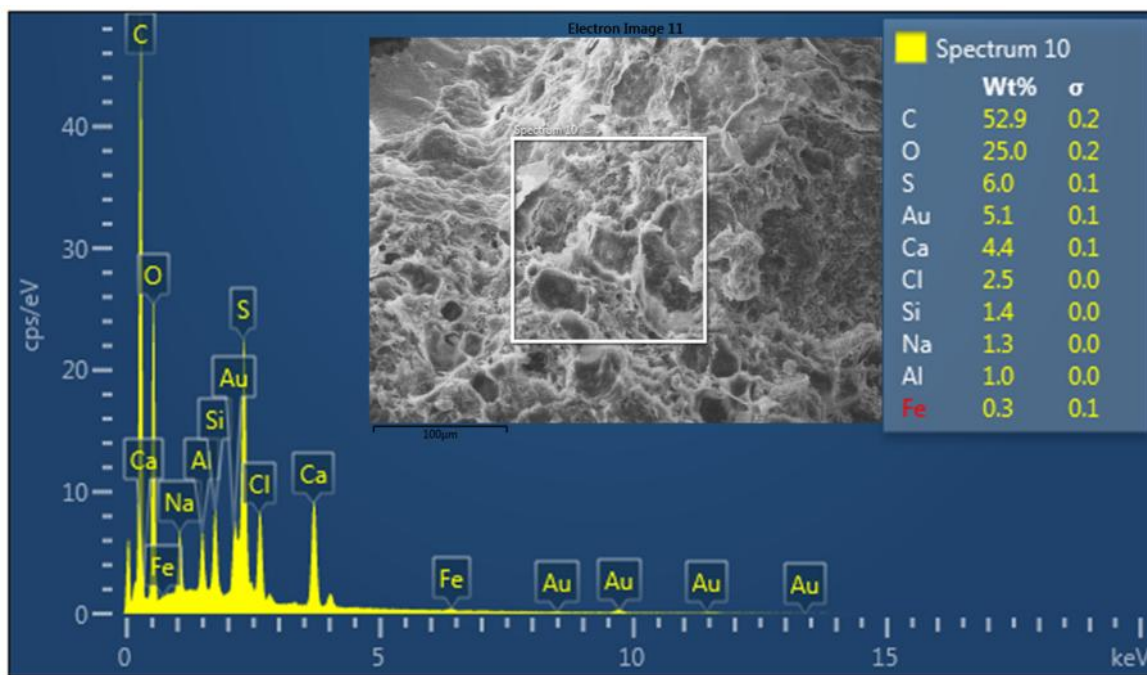


Figure A-4. SEM/EDS 30% Organic content, CaCl_2 , Urea, & 30% SDS – Site 2

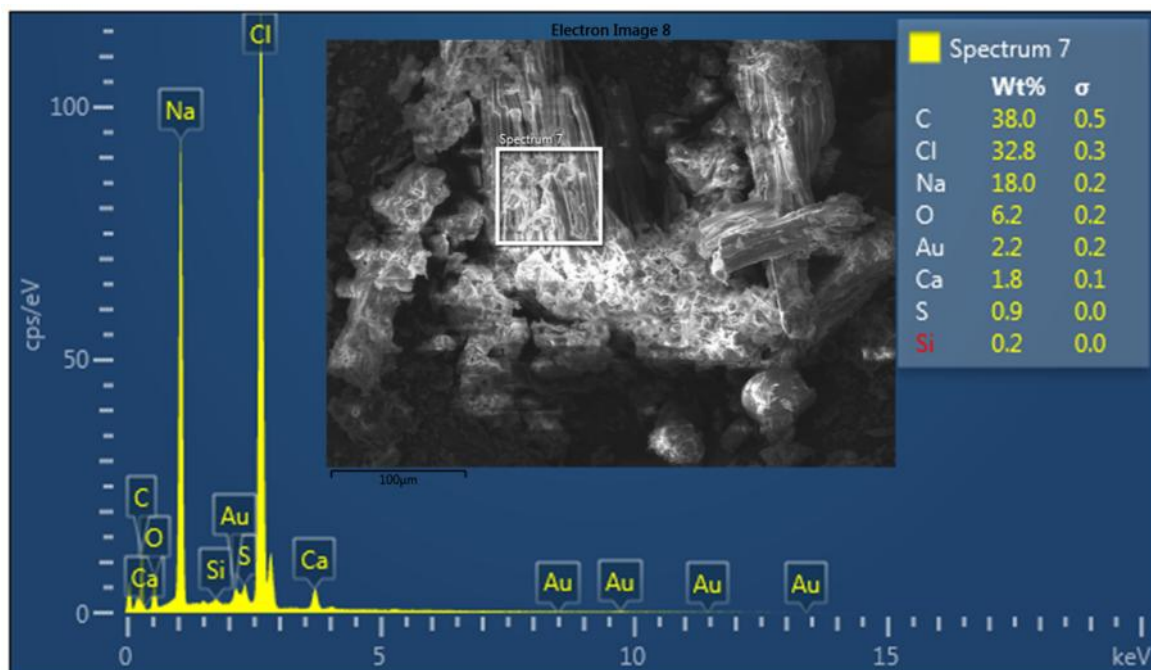


Figure A-5. SEM/EDS 30% Organic content, CaCl_2 , & 30% SDS – Site 2.

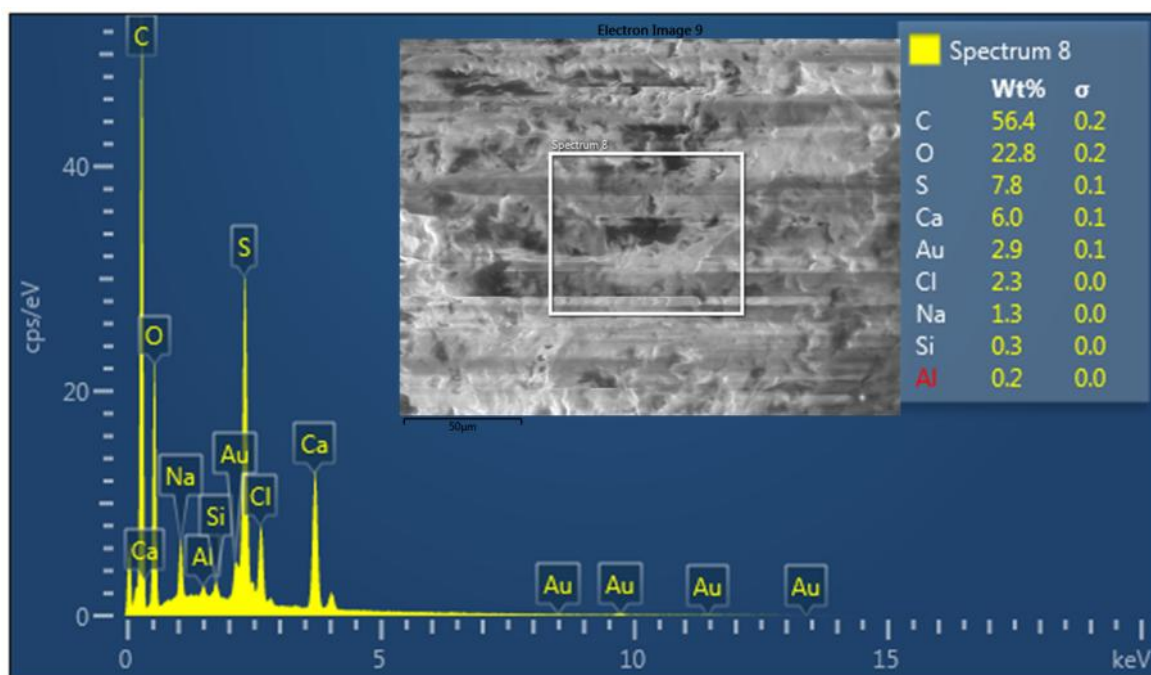


Figure A-6. SEM/EDS 30% Organic content, CaCl_2 , & 30% SDS – Site 3.

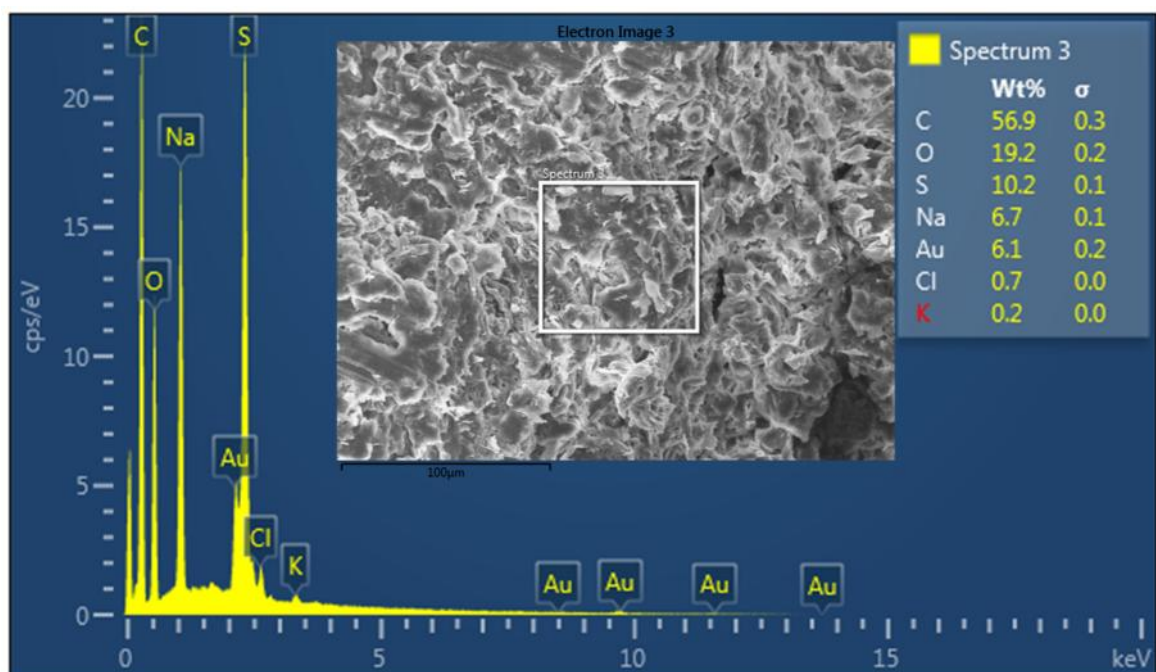


Figure A-7. SEM/EDS 30% Organic content, *Sporosarcina pasteurii*, CaCl_2 , Urea, & 60% SDS – Site 1.

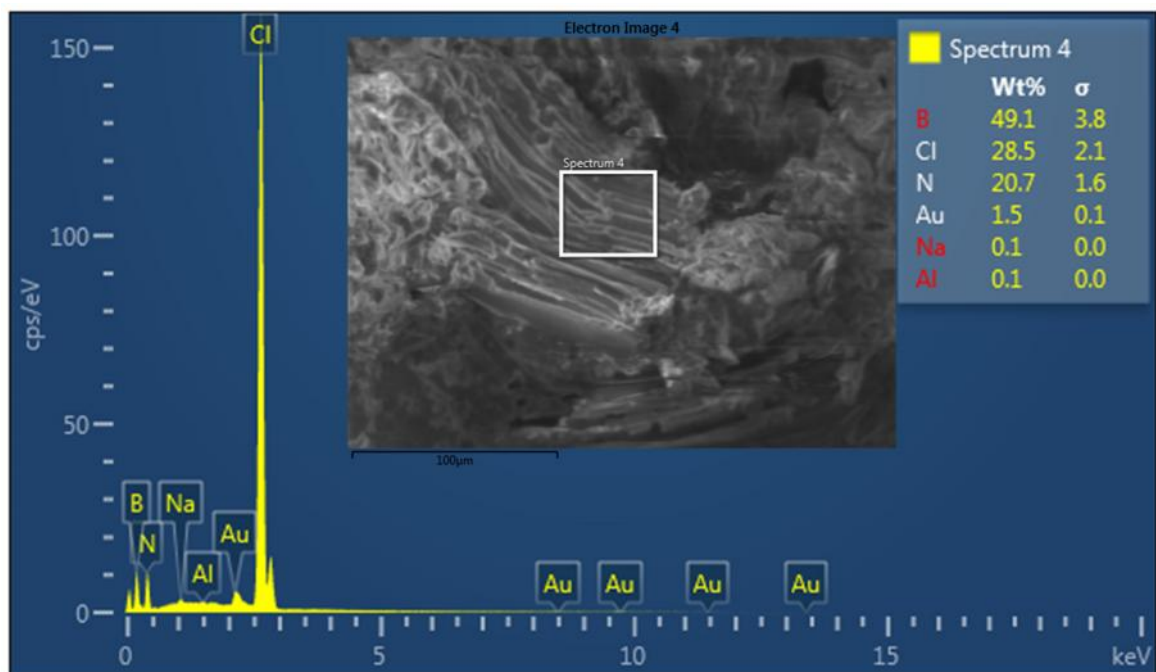


Figure A-8. SEM/EDS 30% Organic content, *Sporosarcina pasteurii*, CaCl_2 , Urea, & 60% SDS – Site 2.

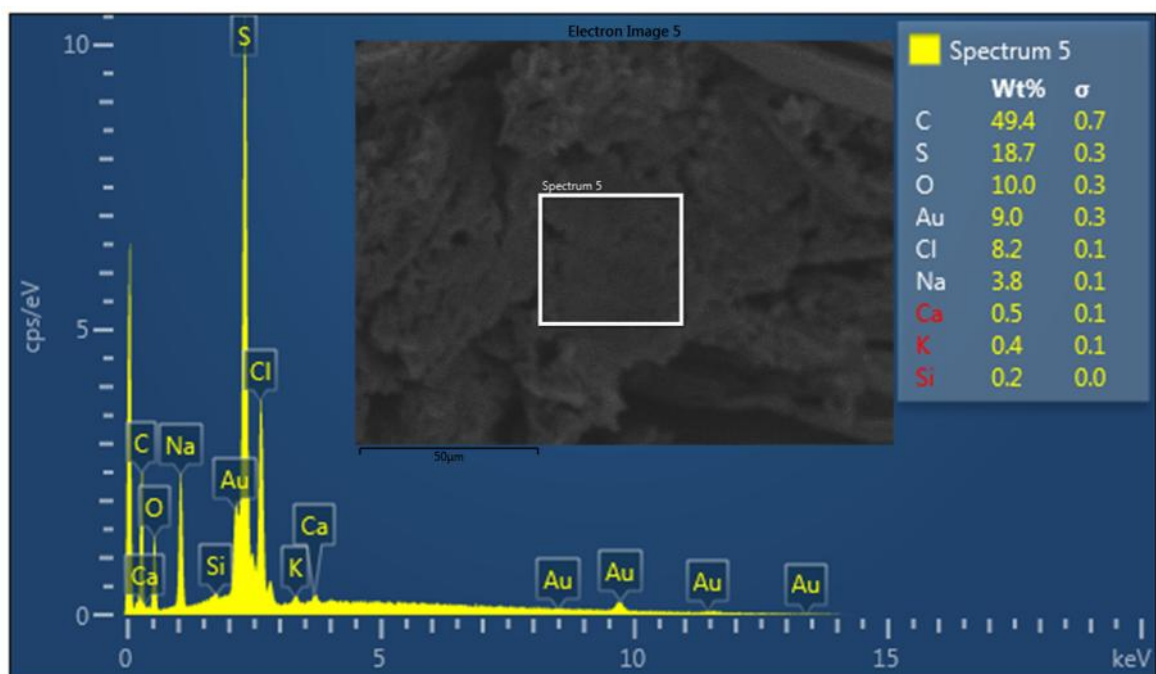


Figure A-9. SEM/EDS 30% Organic content, *Sporosarcina pasteurii*, CaCl_2 , Urea, & 60% SDS – Site 3.

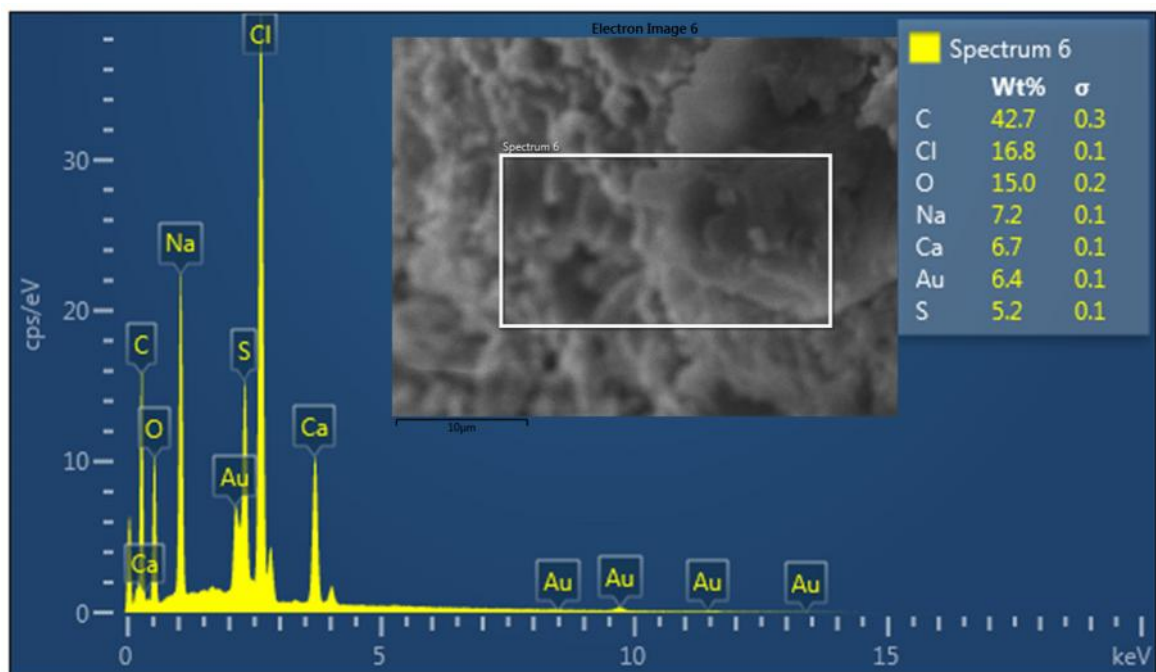


Figure A-10. SEM/EDS 30% Organic content, *Sporosarcina pasteurii*, CaCl_2 , Urea, & 60% SDS – Site 4.

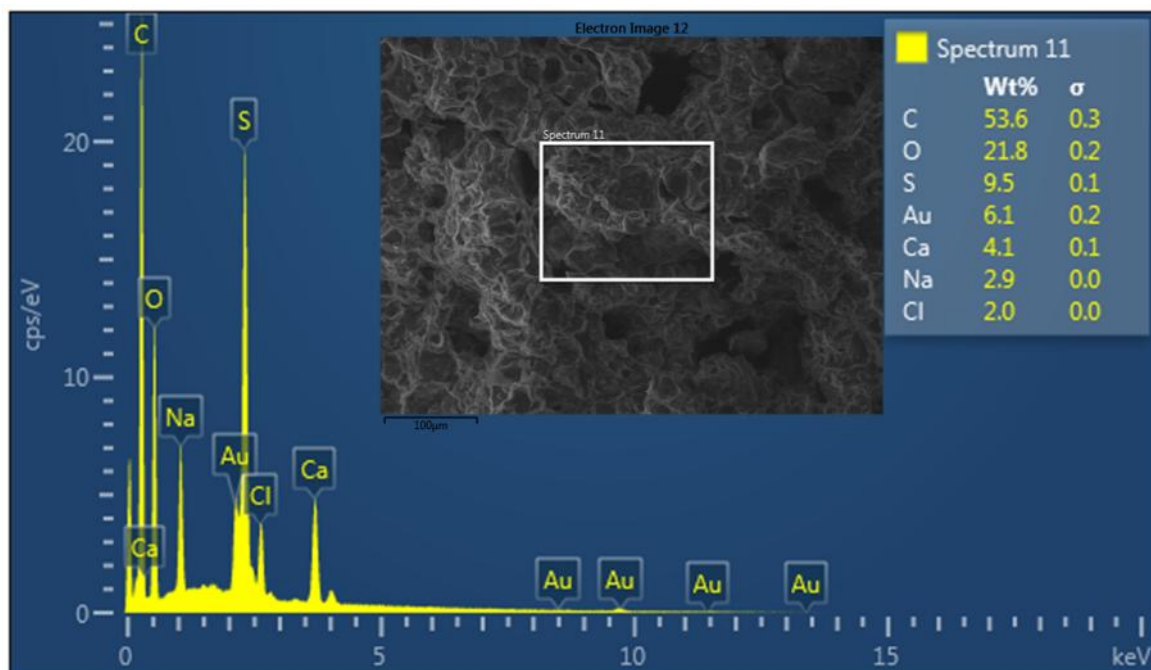


Figure A-11. SEM/EDS 30% Organic content, CaCl_2 , Urea, & 60% SDS – Site 1.

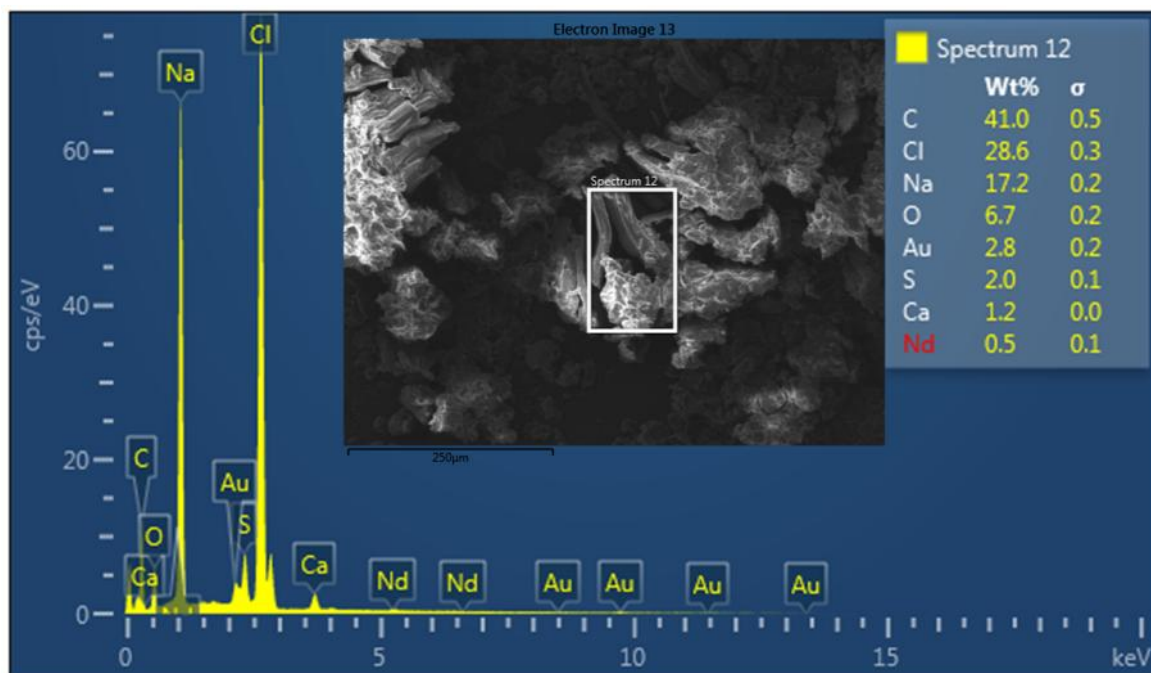


Figure A-12. SEM/EDS 30% Organic content, CaCl_2 , Urea, & 60% SDS – Site 2.

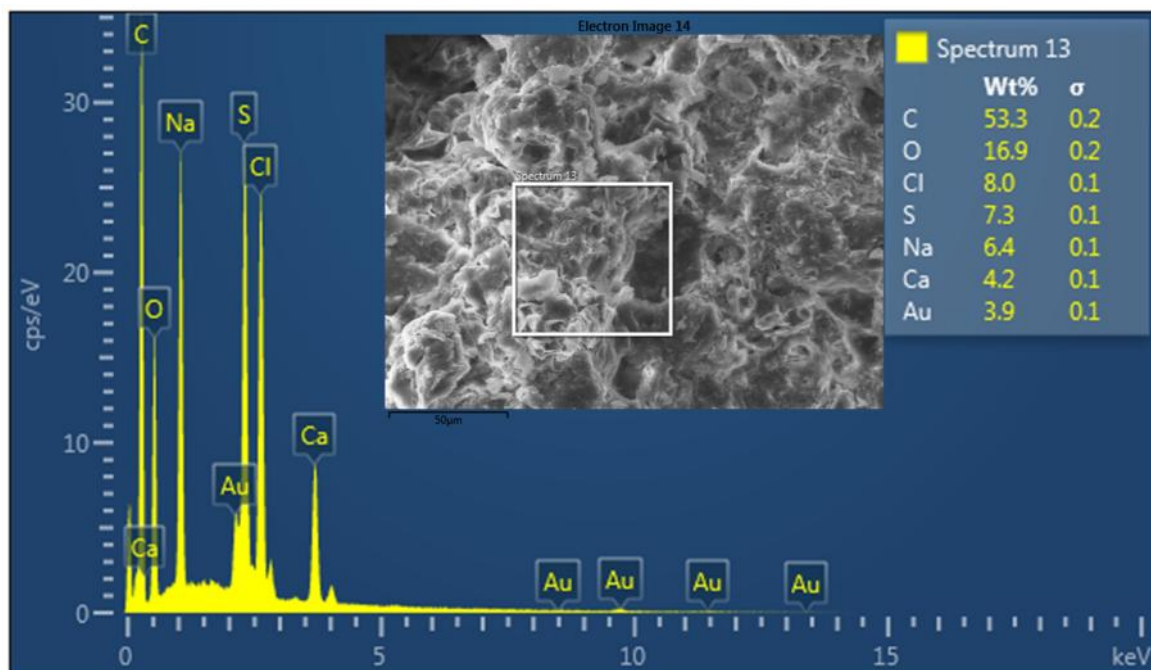


Figure A-13. SEM/EDS 30% Organic content, CaCl_2 , & 60% SDS – Site 1.

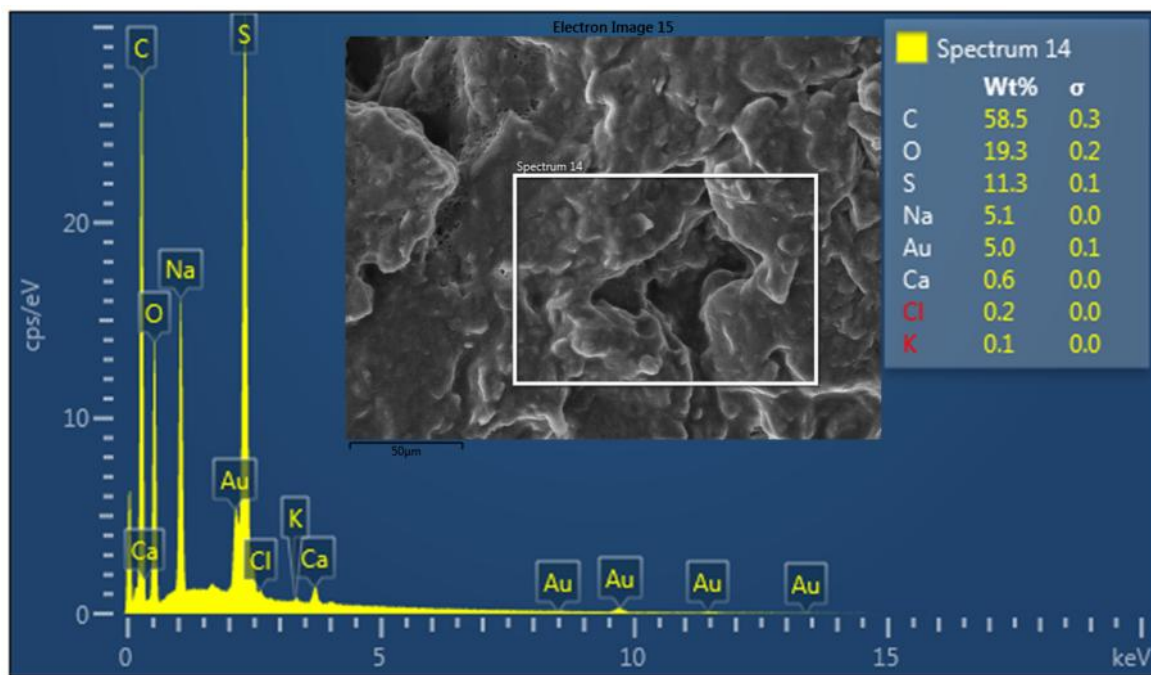


Figure A-14. SEM/EDS 30% Organic content, *Sporosarcina pasteurii*, CaCl_2 , Urea, & 90% SDS – Site 1.

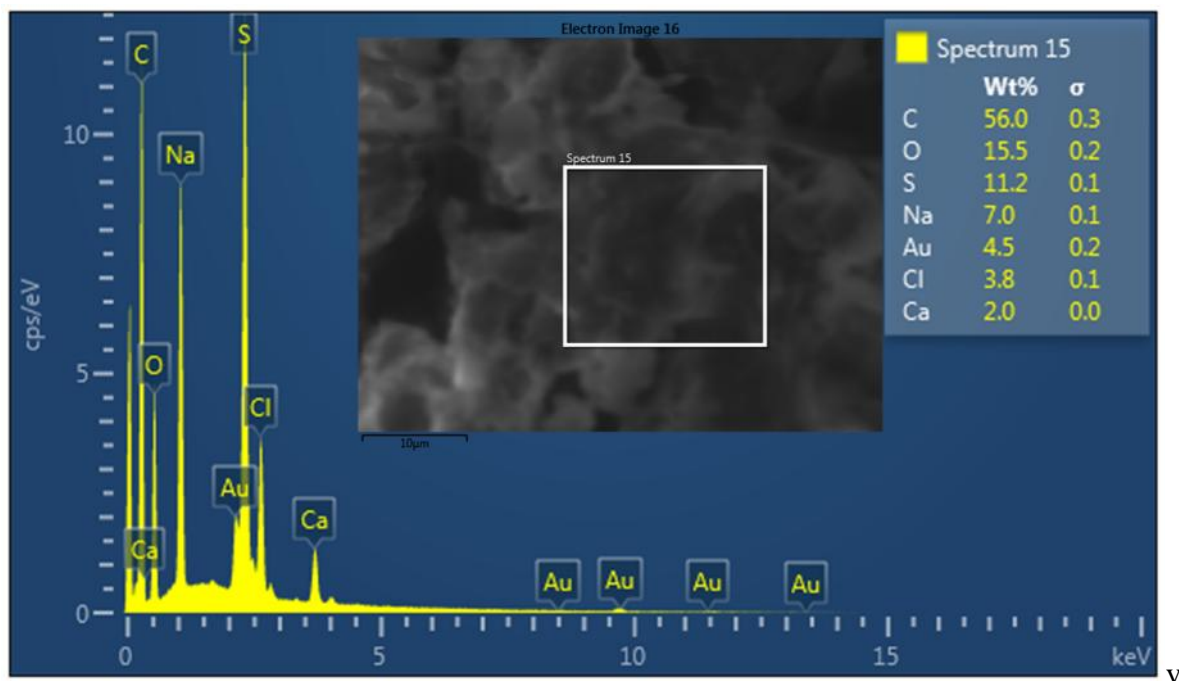


Figure A-15. SEM/EDS 30% Organic content, CaCl_2 , Urea, & 90% SDS – Site 1.

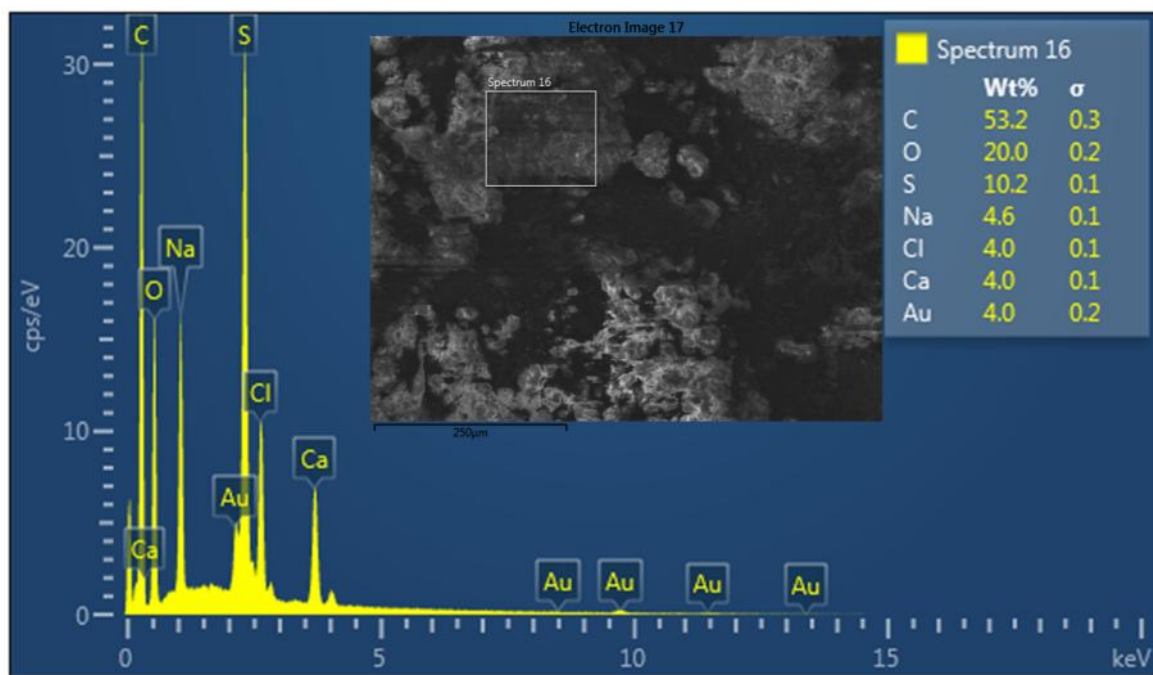


Figure A-16. SEM/EDS 30% Organic content, CaCl_2 , & 90% SDS – Site 1