Stabilization and Strengthening of Fine Oil Sand Tailings using Sodium Silicate

Yixuan Wang, Julie Qiulin Shang & Yu Guo
Department of Engineering– University of Western Ontario, London, Ontario
Michael McDonald, Xianglian Li & Timothy Evans
National Silicates, Toronto, Ontario, Canada

Abstract
The challenge of reducing oil sand tailings ponds are pressing and well known to geotechnical and environmental engineers. Flocculation-based technologies have been the preferred route for the treatment of mature fine tailings (MFT). Solidification of MFT represents an alternative treatment method that can address limitations associated with flocculating-based technologies and allow a treated zone to be trafficable in a much shorter period of time.

This paper explores the potential of sodium silicate and aqueous alkali alumino silicate (AAAS) for the solidification of MFT. Silicates represent a non-traditional class of stabilizers for improving MFT. Past research has focused on the use of Portland cement, geopolymers and limes as solids material that could impart strength to MFT. Alkali silicates were considered worth investigating given their use and properties for the stabilization of soil. As a solid free, low viscosity liquid a silicate-based system would offer certain advantages such as ease of mixing and application compared to solid solidification chemicals.

Résumé
Le défi de la réduction des bassins de résidus de sable bitumineux est urgent et bien connu des ingénieurs en géotechnique et en environnement. Les technologies basées sur la floculation ont été la méthode préféréepour le traitement des résidus fins matures (MFT). La solidification de la MFT représente une méthode de traitement alternative qui peut prendre en compte les limitations associées aux technologies basées sur la floculation et permet à une zone traitée prêt au trafic dans une période de temps beaucoup plus courte.

Cet article explore le potentiel du silicate de sodium et de l'alumino-silicate alcalin aqueux (AAAS) pour la solidification de la MFT. Les silicates représentent une classe non traditionnelle de stabilisants pour améliorer la MFT. Les recherches antérieures ont porté sur l'utilisation de ciment Portland, de géopolymères et de limes comme matière solide pouvant conférer de la résistance à la MFT. Les silicates alcalins ont été considérés méritant d'être étudiés compte tenu de leur utilisation et de leurs propriétés pour la stabilisation du sol. En tant que liquide, à faible viscosité, un système à base de silicate offrirait certains avantages tels que la facilité de mélange et d'application par rapport aux produits chimiques de solidification solides.

1 INTRODUCTION

Extraction of Bitumen from the surface-mined oil sands ores in northern Alberta generates large volumes of tailings with high water content, which are mixtures of clay, silt, sand, residual bitumen and other hydrocarbons (Beier and Sego, 2008; Jeeravipoolvarn et al., 2009). The tailing suspension gradually settle to achieve approximate 30% solid content, known as mature fine tailings (MFT) during the deposition (Siddique et al., 2014; Thompson et al., 2017). The accumulation of MFT and tailing storage ponds exerts significant impacts on the indigenous economics and environment, which compels the oil sands industry to take measures to meet the regulations set forth by the government (Farkish and Fall, 2013; Wang et al., 2014). To increase the density and strength of MFT is likely to be the most important goals for the ongoing treatments (Salam et al., 2016).

Chemical stabilization is one of the soil improvement techniques in geotechnical applications. The process involves the incorporation of additives to the soil with poor engineering properties. The soil stabilizers can be categorized as traditional and non-traditional (Tingle et al., 2007). Reviews of past studies show that the concentrated liquid sodium silicates are one of the non-traditional stabilizers that normally used in chemical grouting on sandy soils (e.g., Sherwood, 1961; Gonzalez and Vipulanandan, 2007; Guo et al, 2017), but the information regarding the improvement of fine-grained geo-materials with silicates is limited. In this study, soluble silicates are used in conjunction with organic setting agents for the treatment of MFT. The objective of this paper is to present experimental results showing the influence of silicate dosages, and short-term curing duration on stabilization of MFT by performing solid content test, undrained shear strength test, plasticity test and scanning electron microscopy (SEM).

1.1 Soluble Silicate Chemistry

Soluble silicates are a widely used chemical that find application in several different industries including;

industrial cleaning, construction, oil & gas, cementing, grouting and as a chemical feedstock. Given the wide and long use of sodium silicates, the chemistry has been documented in the literature. Two highly referenced sources of silicate chemistry and their applications are Iler (1979) and Vail (1952).

As a summary, silicates are typically prepared via a gas-fired furnace using sand and an alkali source to prepare a glass that is subsequently dissolved into water. The chemistry of these soluble silicates is driven by the wt. ratio of SiO_2 to alkali and by the dissolved solids. For example a 3.2 ratio sodium silicate would have 3.2 kg of SiO_2 for every 1 kg of Na_2O. A "3.2" ratio silicate is the most commonly used ratio for geotechnical applications.

The fundamental unit, the silicic acid anion, is shown below in Figure 1, where charges on the oxygen would be balanced by a proton or sodium (in the case of sodium silicate) A unique feature of silicates is that they do not demonstrate monomeric character; rather some 30-40 structures exist in equilibrium in a given liquid product. Figure 2 shows examples of condensed structures derived from the silicate monomer.

A wealth of chemistry is available to the silicate user ranging from simple dehydration (boosting solids as in adhesive or binding applications) to reactions on the anion sites (e.g. use of silicate to convey anionic charge to surfaces via coating, reactions with metals in complexation), to crystallization reactions (such as zeolite synthesis) to neutralization of alkali (as in sol-gel). Additional chemistry can be performed on the silanols (SiOH) in gels via adsorption, ion-exchange, or by reaction with organic ligands such as in silanes. This diversity in chemistry and the relatively good material safety and low cost make silicates a widely appreciated chemical for use in the industries stated above.

Soluble silicate in the form of Aqueous Alkali Alumino Silicate (AAAS) represents a non-conventional form of sodium silicate. AAAS is a pre-primed silicate that includes aluminum dissolved into the silicate. It is a clear soluble liquid silicate that is stable. When this AAAS product is subjected to high shear (via intense mixing) or sheared with other ingredients such as dilution water, the AAAS product will convert to a solid crystalline (Marcus 2012). This liquid-to-solid conversion provides controllable setting and the resulting crystalline material that can show low syneresis (low shrinkage) upon aging and provide for higher bond strengths. Table 1 provides a property comparison of properties of the tested silicates.
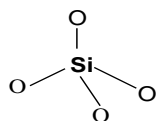

Figure 1. Silicic acid anion monomer (charges not shown)

Figure 2. Condensed silicate anion structures. Dots represent silicon atoms and lines oxygen atoms.

Table 1. Properties of Sodium Silicate Solution

	Na_2O (%)	SiO_2 (%)	Al_2O_3 (%)	Na_2O: SiO_2	Solids (%)
"AAAS"	16.2	27.9	1.6	1.7	45.7
"NS" 3.2 ratio	8.9	28.7	-	3.2	37.6

1.2 Tailing Characteristics

The MFT samples examined were dark brown in colour and had a strong petroleum odor. The main characteristics of MFT are summarized in Table 2. According to the unified soil classification system (USCS), the tailings can be characterized as CL. The liquid limit, plastic limit and plasticity index of MFT is 47.0%, 23.9% and 23.1, respectively. The soil pH is 8.52 and corresponding zeta potential is −38 mV. Figure 3 presents the grain-size distribution curve of the MFT, showing that silt (i.e. 81%) is the predominant particle size. SEM imaging (Figure 4) indicates that the particles of the raw MFT are slightly flocculated, forming a mild edge-to-edge 'card-house' structure.

Table 2. Characteristics of MFT

Parameters	MFT
Specific gravity, Gs	2.31
Water content, W%	185%
Solid content [1], S%	35%
Void ratio, e	4.27
Dry density (Mg/m^3)	0.70
Atterberg limits	
Liquid limit, (%)	47.0
Plastic limit, (%)	23.9
Plasticity index	23.1
USCS classification	CL
Lazer particle size analysis	
D_{25} (µm)	2.93
D_{75} (µm)	17.20
D_{90} (µm)	30.75
Sand (4.75-0.075mm), %	0.00
Silt (0.075-0.002mm), %	81.00
Clay(<0.002mm) %	19.00
Zeta potential (at natural condition)	-38 mV
Natural pH of suspension	8.52
Electrical conductivity, µS/cm	1460

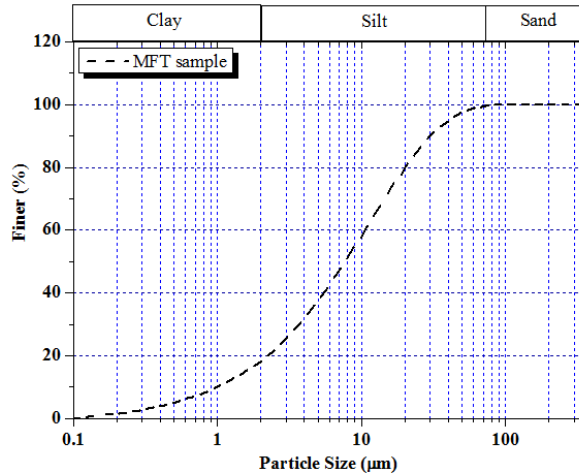Note: [1] Solid content, S%=1/(1+W%), W%=water content

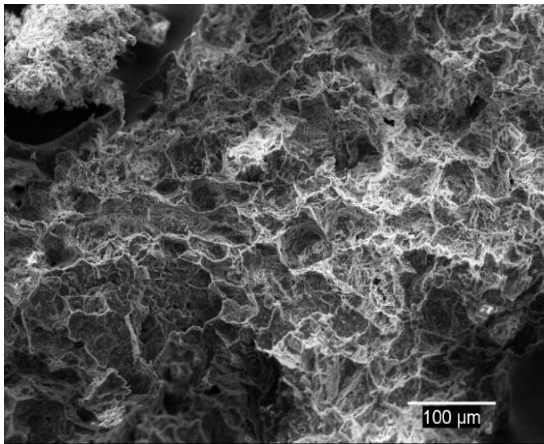Figure 3. Grain size distribution of untreated MFT

Figure 4. SEM picture of untreated MFT (Mag=1,000X)

1.3 Test Procedures & Considerations

In the study, the initial water content (185%) was adjusted to simulate the in-situ water content of MFT in tailing ponds. The samples were dried for 3 days under air-tight condition, then a prescribed amount of deionized water was added. In order to investigate the influence of silicates on MFT, undiluted 3.2 ratio sodium silicate (N® grade) and AAAS with corresponding setting agents were mixed with MFT suspension at different volumetric ratios (v/v), as summarized in Tables 3-4. As shown, the experiment was divided into two groups based on the silicate usage: The high content group (i.e. 30%, 40% and 50% for NS; 40%, 50%, 60% for AAAS) and low content group (e.g., 3%, 5%, 8%, 10% for both N® and AAAS). More details on the determination of the grouting formula can be found in Wang (2017). It is also noted that no setting agent (i.e., propylene carbonate) was required if the volumetric ratio of AAAS got below 40%, as the gel time was controlled to be 4-5 hours.

For preparing the test samples, the chemicals were added through a two-step process. The predetermined quantity of setting agents (e.g., citric acid) was first added to the raw MFT by a pipette and mixed thoroughly by a miniature mixing machine. After that, the predetermined amount of silicate solutions was added and stirred within 5 minutes until a homogenous paste was formed. To prevent the partial accumulation of gels surrounding the impeller blades, the mixing work was carried out rapidly and vigorously. Then the admixtures were transferred to 2'' plastic cylindrical molds (50mm in diameter and 100mm in height). Air bubbles on top surface of the specimens were removed through slight vibrations. Subsequently, all prepared samples were capped and cured under room temperature. After the specified curing time (7, 14 and 28 days), a hole was drilled at the bottom of the molds, then the sample was extracted by air pump for testing (Figure 5).

Table 3. Mixing ratios for 3.2 ratio "NS" sodium silicate - treated MFT sample

Sample ID	MFT (g)	MFT Water (ml)	NS (ml)	Citric Acid (ml)
3%-NS-MFT	200	130	4	2
5%-NS-MFT	200	130	7	2.3
8%-NS-MFT	200	130	11.3	2.4
10%-NS-MFT	200	130	14.5	2.5
15%-NS-MFT	200	130	23	5
30%-NS-MFT	100	65	43.3	36.1
40%-NS-MFT	80	52	69.3	52.0
50%-NS-MFT	30	19.5	72.8	53.3

Table 4. Mixing ratios for AAAS-treated MFT sample

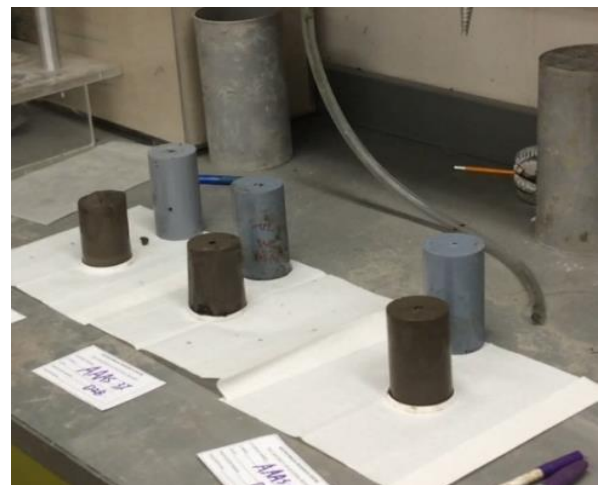| Sample ID	MFT (g)	MFT Water (ml)	AAAS (ml)	Propylene Carbonate (ml)
3%-AAAS-MFT	200	130	4	0
5%- AAAS-MFT	200	130	7	0
8%- AAAS-MFT	200	130	11.3	0
10%- AAAS-MFT	200	130	14.5	0
40%-AAAS-MFT	120	77.9	51.9	0
50%-AAAS-MFT	100	64.91	67.61	2.71
60%- AAAS-MFT	80	51.93	85.1	4.82

Figure 5. Extracted samples

2   RESULTS & DISCUSSION

2.1   Solids Content

The solid content (S%) of MFT is defined as the mass of dry solids to the total mass of MFT, and it is calculated by the water content (W%) of the whole sample determined from ASTM D4959 – 16. The results of S% for NS- and AAAS-treated MFT samples at 7, 14 and 28 days are plotted versus the silicate content in Figure 6 (a) and (b), respectively. As expected, after treatment the solid content of MFT samples increased as silicate content increased. For example, after 28 days, 10%-NS-MFT sample exhibited a solid content of 37.02%, whereas 10%-AAAS-MFT sample showed a higher solid content of 40.95%. The solid contents continued to increase within a short period of time by consuming water for gel formation and water release from gel syneresis. According to the daily weighing, it is known that the amount of water evaporation is negligible. It is also noted that the difference in S% between two silicate-treated MFT samples became more noticeable when the silicate content went up to 40% or higher.
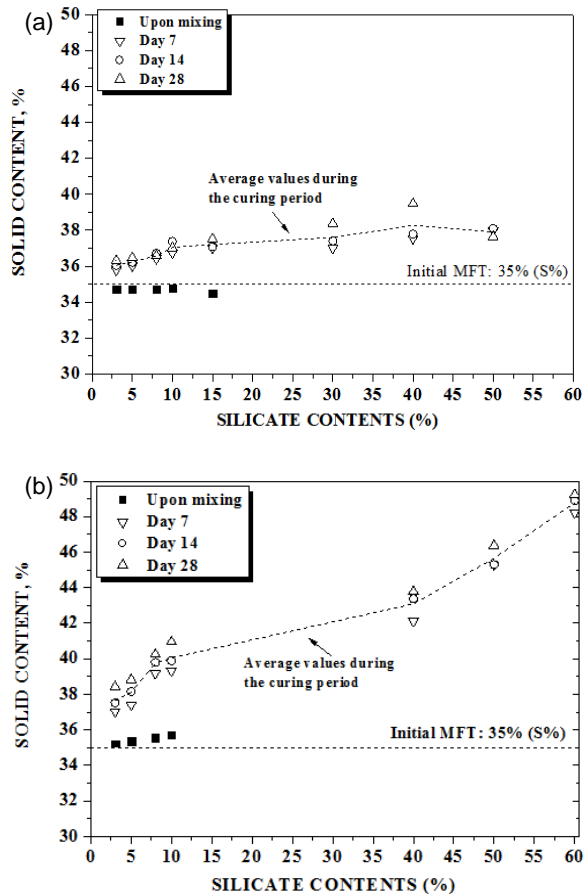
The most significant increase in the solid content was registered in 60%-AAAS-MFT sample at the end of the 28 days, where the sample achieved nearly 50% solid content (i.e. 49.24%). It is noted that after 7-day curing, the solid content of the sample reached up to 48.22%. This indicated that the increase in the solid content was near completion within 7 days. This observation is consistent with other NS-treated MFT samples with varying silicate contents, including 10%- and 50%-NS-MFT samples, as shown in Figure 6 (a).

2.2   Undrained Shear Strength & Sensitivity

The undrained shear strength of MFT samples was evaluated using the Swedish fall cone method (Hansbo, S. 1957). For each sample, a minimum of three cone penetration measurements were taken and the average of the measured values was used for the analysis.

The effects of silicate contents and curing duration on the undrained shear strength (S_u) development of MFT are shown in Figure 7(a) and (b), respectively. Figure 7(a) reveals that the S_u of MFT samples increased with the increasing NS and AAAS contents. It is also noted that for NS-treated MFT samples, at least 5% of silicate content was needed to cause a strength increase. After 28 days, the S_u of 10%- and 15%-NS- MFT samples reached 4.83 and 7.55 kPa, while the specimens treated with 5% and 8% AAAS reached 4.8 and 5.5 kPa of Su, respectively. These data suggested that, the undrained shear strength of 5 kPa, a one-year minimum requirement for the MFT treatment (Directive 074 (2009)), was achieved in a short duration. In particular, all MFT samples treated at high silicate contents showed a strength gain in excess of 10 kPa. It should be mentioned that this value (10 kPa) of S_u was a five-year criterion of MFT depositions regulated by Directive 074 (2009).

Furthermore, as illustrated in Figure 7(b), for all MFT samples treated by low contents of silicates (i.e. 3%-10% for NS and AAAS), the S_u exhibited an initial increase at first 7 curing days but did not further increase with time. This was consistent with the solid content results shown before, indicating that most chemical reactions between MFT and silicate grouts completed within 7 days. For MFT samples treated by high contents of NS (e.g. 30-50%), a sharp strength increase in the second cuing period (7 to 14 days) and a relatively slow increase at the later stage (14 to 28 days) were observed. On the other hand, for MFT samples treated by high contents of AAAS (e.g. 40-60%), the strength gain was nearly completed after 7 days. This suggested that the strength development of AAAS-treated MFT samples was more rapid than the NS-treated samples at high silicate content levels.

Figure 6. (a) Solid contents of NS-treated MFT and (b) Solid contents of AAAS-treated MFT
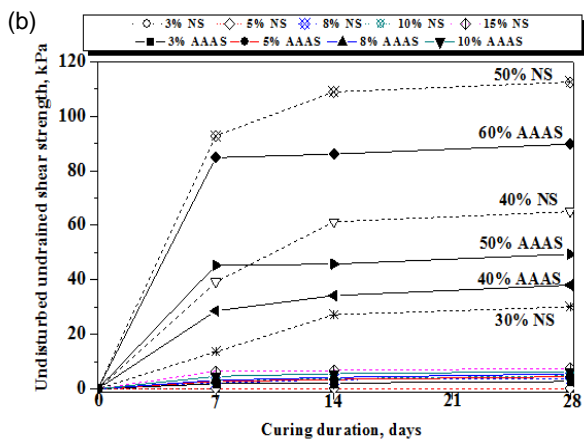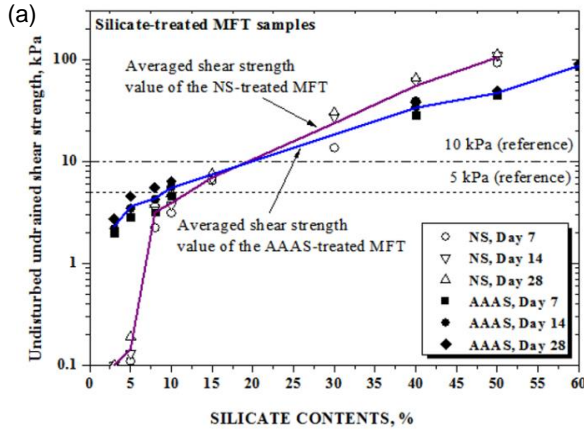
Figure 7. (a) Dosage effect and (b) Curing time effect on the undrained shear strength gain of treated MFT

Figure 8(a) and (b) presents the sensitivity results of the silicate-treated MFT samples. As shown, the sensitivity of all MFT samples treated by silicates at low contents varies in the range of 1 to 4. However, there was a significant increase in sensitivity values (St=4-16) on samples treated with high silicate contents (e.g. 50% for NS and AAAS). In general, the sensitivity of AAAS-treated MFT samples was lower than that of NS-treated MFT samples at same silicate dosage rates.
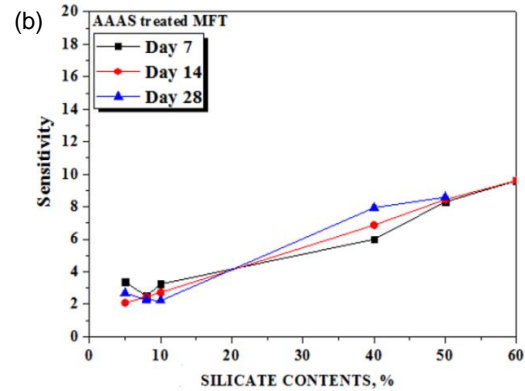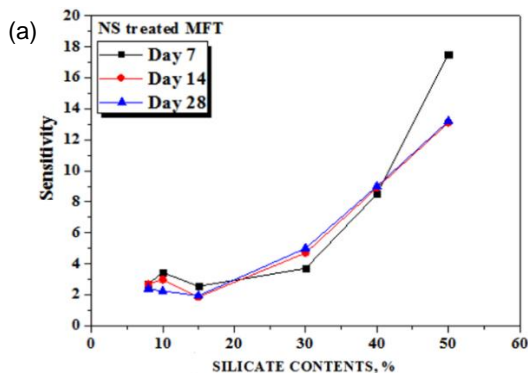
Figure 8. Sensitivity of (a) NS-treated MFT sample and (b) AAAS-treated MFT sample

2.3 Plasticity

The Atterberg limits of silicate-treated MFT samples were determined by Casagrande percussion cup method and thread rolling method (ASTM D4318-10). The typical test results are presented in Figure 9(a) and (b). After the silicate treatments, both the liquid limit (LL) and plastic limit (PL) increased. The highest increase in the LL occurred in the sample mixed with 15% NS, attaining a peak value of 174.4% after 28 days. Under the same conditions (i.e., curing time, silicate content), the magnitude of the LL increase in AAAS-treated MFT samples was found to be lower than that of NS-treated MFT samples. The increase in the LL in all silicate-treated MFT samples was believed to be associated with changes in the geometric arrangement of particles and entrapped water in pore spaces between MFT particles. It is also noted that at the end of the curing period, the PL of 15%-NS-MFT sample reached 77.4%, and this was approximately two times greater than that of the untreated MFT sample (23.9%). However, the PL of AAAS-treated MFT samples did not change significantly with elevating AAAS contents.
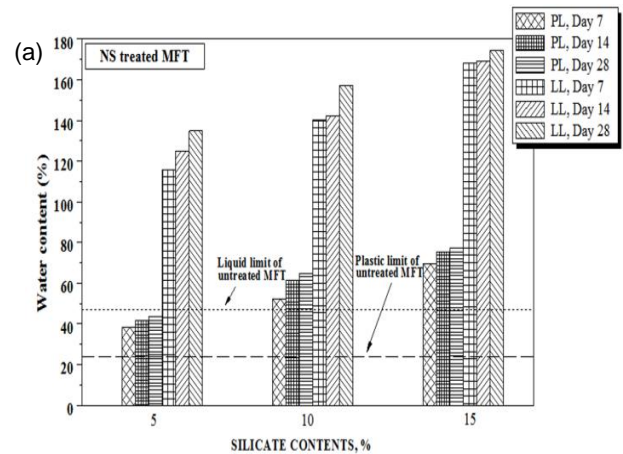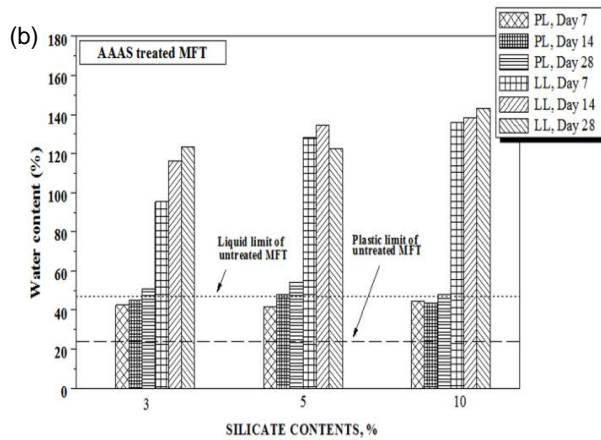
Figure 9. Atterberg limits of (a) NS-treated MFT sample and (b) AAAS-treated MFT sample

Figure 10 is a plasticity chart showing the plasticity of treated MFT samples. It is found that, the points of AAAS-treated MFT samples (3%, 5% and 10%) on the chart moved upwards over the A-line, while for the NS-treated MFT samples (5%, 10% and 15%), the points shifted below the A-line. This indicated that MFT samples typically behaved as inorganic silts of high plasticity (MH) after NS treatment, while the MFT samples treated by AAAS behaved as inorganic clays of high plasticity (CH).
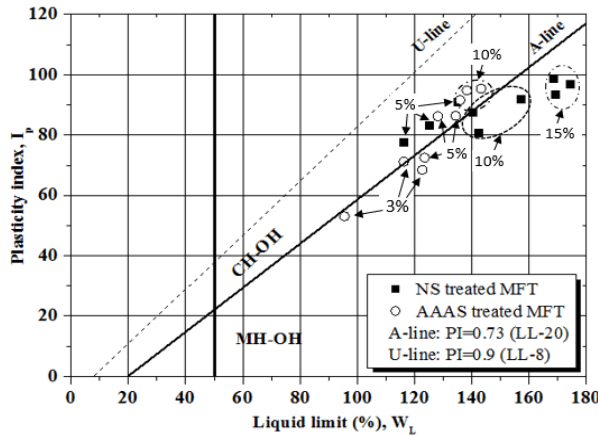

Figure 10. Casagrande plasticity chart

2.4 Scanning Electron Microscopy (SEM)

To examine the micromorphological changes in the stabilized MFT, SEM imaging was employed on the selected samples. SEM samples were prepared by following the procedures suggested in a study (Azam, 2012). The samples were dried rapidly by freeze drying method using liquid nitrogen. The fabrics were characterized at a magnification of 2,000x at 10kV.

Figures 11(a)-(c) and Figures 12(a)-(c) provide the SEM photos of the MFT samples mixed with 5%, 10% and 40% NS and AAAS at curing age of 28 days, respectively. As shown in Figure 11(a), MFT samples treated by 5% NS exhibited a fairly open microstructure, with the solid particles assembled in a random orientation. As a result of an increase in NS content to 10%, the flocculation of solid particles was evident, as seen in Figure 11(b). On the other hand, less distinct pores and relatively compact matrix are observed in MFT samples treated by 5% AAAS (Figure 12(a)). It appears that discrete particles were covered by gel-like amorphous substances, giving rise to the hazy patches around particles. Figure 12(b) shows that the particles were significantly coated by 10% AAAS gels, forming larger clusters.

Figure 11(c) depicts a distinct network structure on the MFT sample after 40% NS treatment. The NS gels formed the chemical crosslinks between solid particles with some sign of reticulation, and the microstructure of the entire NS-treated MFT sample emerged as a crusty web. In contrast, solid particles in the 40%-AAAS-MFT sample were well-bonded together in a packet fabric, as shown in Figure 12(c). The AAAS gel appeared to have irregular shapes and vague outlines, and the pores of the specimen are less visible in comparison with Figure 11(c). This suggested that AAAS gel had better space-filling effects on MFT than NS gel with the same dosages.

Comparing the SEM images between the original (Figure 4) and solidified MFT samples, it is observed that the surface morphology of original MFT was modified through silicate treatments. The NS gel (especially in Figure 11(c)) connected the solid particles, while AAAS gel (especially in Figure 12(c)) encapsulated the particles and filled the porous areas inside the mixture. This results in a stronger aggregate of particles and a denser microstructure of MFT. Hence, the mechanical properties (e.g., undrained shear strength) of MFT are improved.
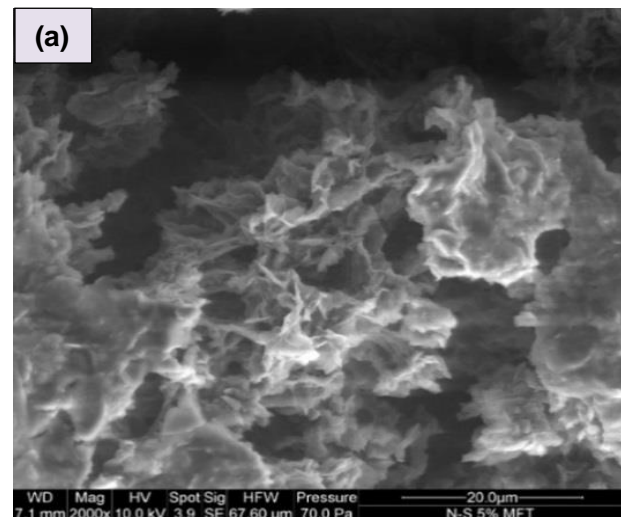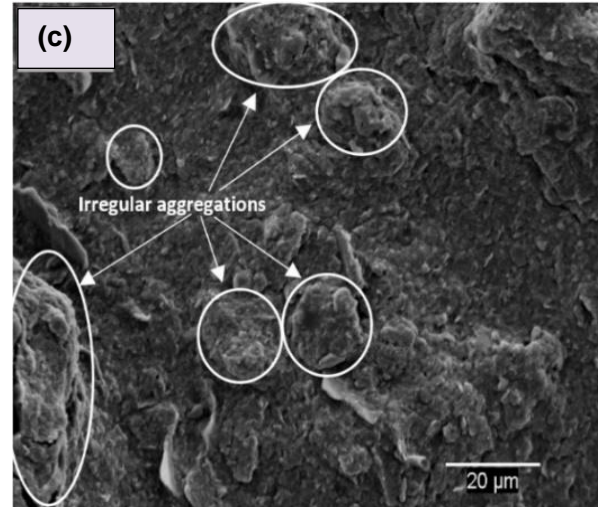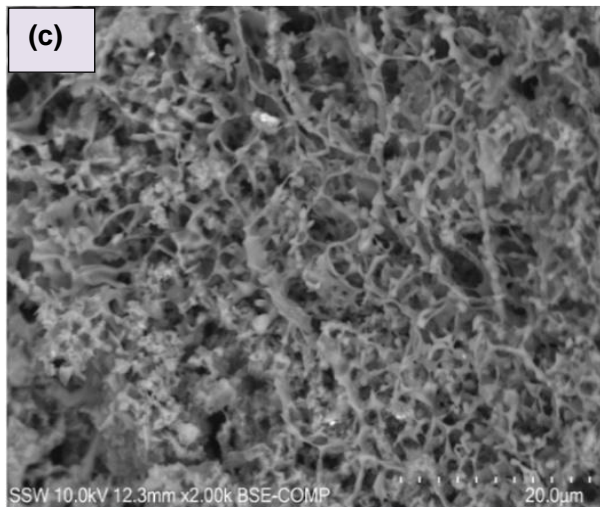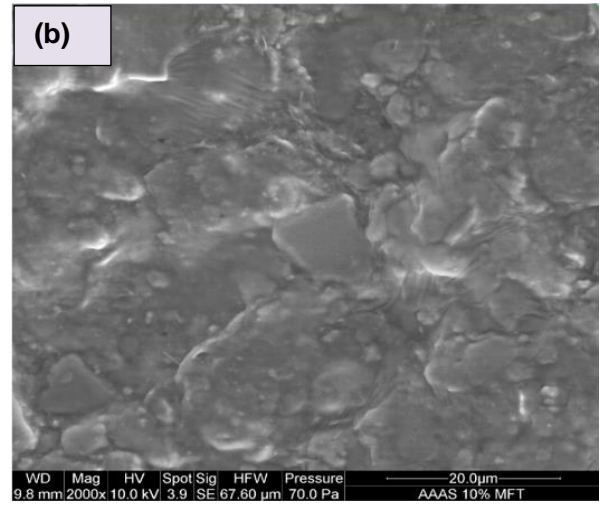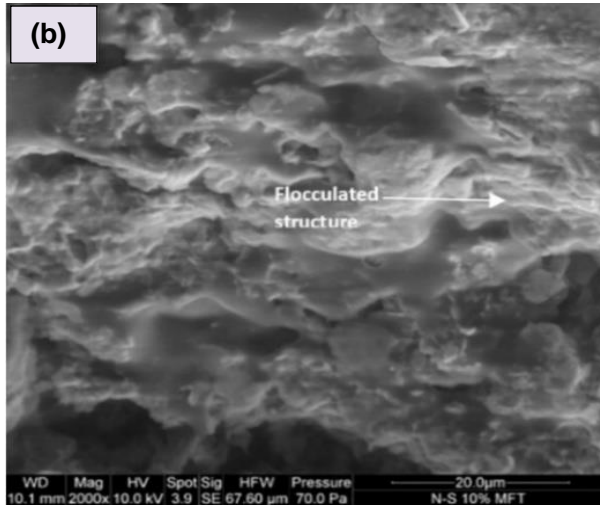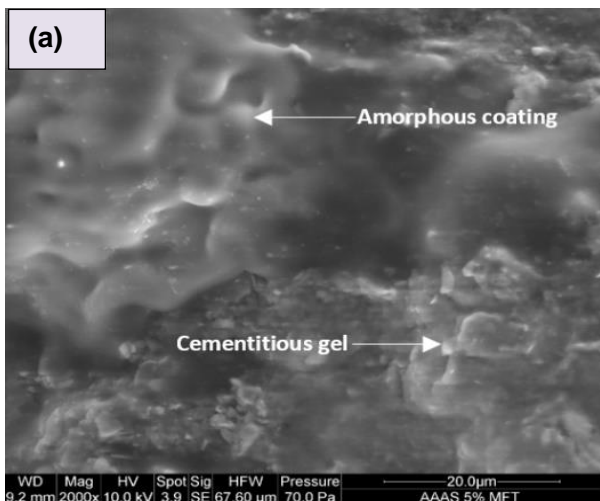
Figure 11. SEM photos after 28-day curing (Mag=2000x). (a) 5% and (b) 10% and (c) 40% NS-MFT;

Figure 12. SEM photos after 28-day curing (Mag=2000x). (a) 5% and (b) 10% and (c) 40% AAAS-MFT;

3   Conclusions

Laboratory tests were performed to measure the engineering properties of silicate-treated MFT. In general, the undrained shear strength, Atterberg limits and solid content of the silicate-stabilized MFT samples increased with silicate contents and curing time. The predominant effect of silicate treatment of MFT is the strength gain, whereas the increase in the solid content is secondary. It is also found that the improvement of MFT properties was most significant in the first 7 days of curing. The micro fabrics of MFT samples were characterized by SEM. Based on the results, several conclusions are presented as follows:

● After 28 days of curing, an undrained shear strength value (5 kPa) can be achieved by adding 15% NS (7.55 kPa) or 8% AAAS (5.5kPa). The sensitivity of NS-

treated MFT samples is higher than that of AAAS-treated MFT samples.

● AAAS is more effective than NS in increasing the solid content of MFT at same curing period. The most significant increase in solid content (49.24%) is registered in MFT sample treated by 60% AAAS at 28 days.

● The MFT samples typically behaved as inorganic silts of high plasticity (MH) after NS treatment, while the MFT samples behaved as inorganic clays of high plasticity (CH) after AAAS treatment.

● The amorphous gel-like substances play an important role in creating bonds between MFT particles and filling the voids between grains. The microstructures of MFT samples become denser and the mechanical properties are enhanced after silicate treatments.

Acknowledgements

References

ASTM D4318-10. Standard test methods for liquid limit, plastic limit, and plasticity index of soils. *ASTM International*, West Conshohocken, PA, 2007, DOI: 10.1520/D4318-10.

ASTM D4959-16. Standard Test Method for Determination of Water Content of Soil By Direct Heating, *ASTM International*, West Conshohocken, PA, 2016, DOI: 10.1520/D4959-16.

Azam S (2012). Effect of composition and morphology on self-weight settling of laterite ore slurries. *Geotechnical & Geological Engineering.* 30(1):107-118.

Beier, N., Wilson, W., Dunmola, A., Sego, D., 2013. Impact of flocculation-based dewatering on the shear strength of oil sands fine tailings. *Can. Geotech. J.* 50 (9), 1001–1007

Directive 074 (2009). Tailings performance criteria and requirements for oil sands mining schemes, *Energy Resources Conservation Board (ERCB), Alberta*

Farkish A, Fall M. (2013) Rapid dewatering of oil sand mature fine tailings using super absorbent polymer (SAP). *J Minerals Eng;*50(51):38–47.

Gonzalez, H. and Vipulanandan, C. (2007), "Behavior of a sodium silicate grouted sand", *Proceedings of Geo-Denver 2007,* Denver, CO, USA, February, pp. 1-10

Guo Y, Shang JQ, Xue B, McDonald M, Li X, Evans T. "Stabilization of Geomaterials using an Innovative Form of Sodium Silicate", *Canadian Geotechnical Conference, Ottawa, October 2017.*

Hansbo, S. 1957. A new approach to the determination of the shear strength of clay by the fall cone test. *Proceedings of the Royal Swedish Geotechnical Institute,* Stockholm, NO. 14.

Iler, R.K. 1979. *The Chemistry of Silica.* New York; John Wiley and Sons.

Jeeravipoolvarn, S., Scott, J.D., Chalaturnyk, R.J. (2009) 10 m standpipe tests on oil sands tailings: long term experimental results and prediction. *Canadian Geotechnical Journal,* 46:875-888

Marcus, A. 2012. Xray Diffraction Analysis of Reacted AAAS Silicates, PQ Corporation, Valley Forge, PA (unpublished).

Salam, A.M., Örmeci, B., Simms, P.H., (2016) Determination of the optimum polymer dose for dewatering of oil sands tailings using UV–vis spectrophotometry. *J. Petrol. Sci. Eng.* 147, 68–76.

Sherwood, T.P. (1961) Soil stabilization by the Use of Chemical Admixtures: A Review of the Present Position. *Roads and Road Construction,* Vol.39, No. 460, pp. 102-110.

Siddique, T., Kuznetsov, P., Kuznetsova, A., Li, C., Young, R., Arocena, J.M., Foght, J.M., (2014b) Microbially-accelerated consolidation of oil sands tailings. Pathway II: solidphase biogeochemistry. Front. *Microbiol. 5 (Article 107).*

Thompson, D.K., Motta F.L., Soares J.B.P., (2017) Investigation on the flocculation of oil sands mature fine tailings with alkoxysilanes. *Miner.Eng.111. 90-99.*

Tingle JS, Newman JK, Larson SL, Weiss CA, Rushing JF (2007) Stabilization mechanisms of nontraditional additives. *Transp Res Rec:* J Transp Res Board 1989(1):59–67

Vail, J. G. 1952. Soluble Silicates, Their Properties and Uses, volume 1. New York: Reinhold. Chemistry, ACS Monograph 116.

Wang, C., Harbottle, D., Liu, Q., Xu, Z., (2014) Current state of fine mineral tailings treatment: a critical review on theory and practice. *Miner. Eng. 58, 113–131.*

Wang, Y. (2017). A study on chemical stabilization of Oil Sands Mature Fine Tailings. *Master thesis, University of Western Ontario*, London, Ontario, Canada.