Strength Development and Reaction Kinetics In Lime-treated Clays

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ABSTRACT

This study reports on the thermodynamics and kinetics of the cementitious reactions between two pure clay minerals (sodium bentonite and kaolinite) and slaked lime. The optimum moisture content (OMC) for strength development was first investigated for each mineral, through an evaluation of both the proctor compaction curves and the 7-day Unconfined Compressive Strength (UCS) results. Particle size of kaolinite was observed to have little influence on the 7-day UCS of specimens treated with 5% slaked lime or 5% Portland cement. A water content dry of optimum was observed to generate the highest UCS values for two different particles sizes of kaolinite, for both the binders. Conversely, bentonite yielded higher UCS wet of optimum (1.4 times the OMC) for both cement and lime. Long term strength tests for the lime blends up to 180-360 days showed that bentonite mixed with 8% slaked lime plateaued at 400 kPa after 28 days of curing. The pore solution extract indicated that pH dropped from 13 to 10 within the same time frame, then remained constant. The Thermogravimetric analysis (TGA) analysis confirmed that this trend was associated with a rapid consumption of free lime. Conversely, kaolinite maintained a pH of 13 up to 180 days and free consumption of lime was gradual. The strength increased almost linearly with time in kaolinite, and the rate of increase was in step with the apparent rate of calcium silica hydrate (CSH) formation. Future work includes full pore solution analysis as well as quantitative analysis of the solid with Nuclear Magnetic Resonance (NMR) and X-Ray Diffraction (XRD) to enhance the TGA data. The solid and pore solution data will be combined to obtain a full kinetic quantitative model for the two minerals.

INTRODUCTION

The most frequent method of clay soil stabilization continues to be the addition of cementitious materials such as lime (CaO), which creates strongly alkaline pH and alters the mineralogy and structure of the soil, producing cement compounds (Calcium Silicate Hydrates and Calcium Aluminate Hydrates or CSH/CAH) and thereby increasing its strength and reducing its swell potential. Lime is often substituted with Portland cement, fly ash or other cementitious materials such as granulated blast furnace slag or cement kiln dust. The addition of the pozzolans is either done on the basis of common industry standards, e.g. 5-8% lime (Hausmann, 1990), or is chosen after treatability studies are performed to determine the optimal dosage; for example, different combinations of pozzolans are tested for mechanical properties such as strength at 28 days of curing to meet a set of criteria dictated by the project design. Even though it is known that different clays react differently and that strength development is a function of time, the type of soil and the pozzolan, there is no quantitative understanding of the fundamental reactions that drive cementitious product formation over time, and the relationship of these to strength development.

Recently, several studies attempted to quantitatively describe clay soil stabilization for pure minerals, namely kaolinite and bentonite (Chrysochoou 2014, De Windt et al. 2014 and Maubec et al. 2017), as well as actual soils (Deneele et al. 2016, Guidobaldi et al. 2017). These studies utilized microstructural techniques such as X-ray Diffraction (XRD), Thermogravimetric Analysis (TGA) and Nuclear Magnetic Resonance (NMR) in a quantitative way, in a departure of the more widespread approach of qualitative observing mineralogical changes over time. Chrysochoou (2014) observed a strong correlation between UCS and dry unit weight for a given soil stabilizer blend and curing time. It was also observed that there is a logarithmic relationship between the increase of amorphous content in clay and strength development of the stabilized clay over time. Maubec et al. (2017) studied the strength evolution of kaolinite and calcium bentonite over time. It was observed that with time, lime stabilization of bentonite gains strength linearly with the formation of CSH and CAH. In kaolinite the strength gain and formation of the chemicals are slower and also affected by higher temperature (50ºC). In the latest study on quantitative soil stabilization involving bentonite, De Windt et al. (2014) suggested with evidence from kinetic model data that the alkaline condition in the system initiates the formation of CSH and CAH where the rate limiting step is controlled by Si availability. They also found that at higher temperature (50ºC) the pozzolanic reactions occurred at a higher rate than at 20ºC. In that study, the solution analysis was accomplished using batch tests of blended materials for different curing times.

A full geochemical model requires a quantitative understanding of the pore solution under in situ conditions, as batch tests induce a substantial amount of dilution, reducing the capacity to evaluate phase stability. The present study attempts to evolve the approach adopted by the aforementioned studies by integrating pore solution extraction to the experimental suite of techniques required for a full geochemical model.

MATERIALS AND METHODS

Three clays were tested: Wyoming sodium bentonite (B), obtained from Bentonite Performance Minerals (product BARA-KADE) and two kaolinites with different particle sizes, obtained from KaMin Performance Minerals (K35, average particle size 7.0 μm and K90 average particle size 1.5 μm as provided by the manufacturer). The K90 kaolinite is the same one used in the 2014 study by Chrysochoou (Chrysochoou 2014). Atterberg limits, hydrometer testing and X-ray Diffraction (XRD) analysis were performed as baseline characterization of the three materials, shown in Table 1.

The chemical composition of the clays are provided in Table 2. The two kaolinite materials contained pure kaolinite mineral according to the XRD analysis, while the bentonite source included approximately 20% of accessory minerals including zeolite (Na-clinoptilolite), quartz, cristobalite, feldspar and mica. This composition is consistent with the SWy-2 source clay mineral of Wyoming bentonite (Chipera and Bish 2001). Two binders were used in the first stage of the study, type I/II Portland Cement (PC) and slaked lime (SL). The PC was obtained from Lehigh, Heidelberg Cement group. The slaked lime was obtained from Fisher Scientific; the chemical is mostly composed of $Ca(OH)_2$ (95%+) with some impurities.

Table 1. Characteristics of three clays

Clay	Bentonite	K35	K90
Liquid Limit	384	27	37
Plastic Limit	68	21	24
Percent <2 µm	75	40	85
Percent <10 µm	85	79	100
Percent <75 µm	90	90	100
Mineralogy	Na-montmorillonite (~80%), Na-clinoptilolite, quartz, cristobalite, anorthite, muscovite	kaolinite	kaolinite

Table 2. XRF analysis of K90, K35 and Na-bentonite

	K90 (wt.%)	K35 (wt%)	Na-Bentonite (wt.%)
SiO_2	51.712	52.682	66.266
Al_2O_3	45.400	45.429	21.056
Na_2O	0.309	0.185	2.550
Fe_2O_3	0.633	0.457	4.792
P_2O_5	0.094	0.079	0.054
SO_3	0.184	0.101	0.562
K_2O	0.077	0.203	0.738
MgO	0.036	0.029	1.824
CaO	0.029	0.021	1.734

Each clay was mixed with 5% binder and subjected to a standard Proctor test (ASTM 2007a). The optimum moisture content (OMC) from each compaction curve was then used to measure strength after 7 days of curing time at four water contents: for the two kaolinites 0.8, 1, 1.2 and 1.4 times the OMC and for bentonite, 1.2, 1.4 and 1.6 times the OMC. This was necessary because the bentonite PC and SL mixes were clearly more brittle and difficult to compact at water contents below the OMC. For bentonite, a sample with 8% lime and 40% water content was also tested to explore the effect of lime percentage on the strength of the sample. The Unconfined Compressive Strength test (ASTM 2007b) was performed for triplicate specimens and UCS-water content curve was prepared to compare the results with the compaction curve results for maximum dry density.

The combined results of the compaction and 7-day UCS tests were used to select a single water content for B and K90 to prepare samples for longer curing times, up to 720 days for strength and geochemical analysis tests. Na-bentonite was mixed with 8% SL at 40% water content and K90 with 5% SL at 30% water content using a mechanical concrete mixer. Samples were compacted according to the standard Proctor protocol, sealed with parafilm and stored inside plastic bags at 95% humidity. Selected results of quadruplicate samples up to 180 days of curing for kaolinite and 360 days for bentonite are shown in this study.

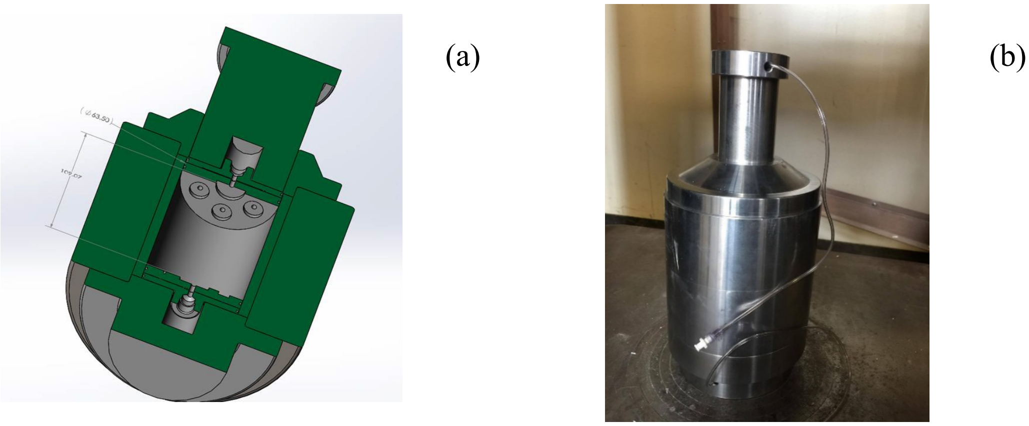

Figure 1. Custom made squeezing apparatus, cross section of pressure chamber (a), assembled apparatus (b)

For each curing time, the quadruplicate samples were tested for UCS. The UCS breaks were used to conduct moisture content analysis and obtain pore water solution using a custom made apparatus. The apparatus is shown in Figure 1, along with a cross section of the pressure chamber.

The design was based upon extraction devices used for rock and concrete samples (Cyr et al 2008). It consists of a cylinder (pressure chamber), a bottom plate, a piston and a guiding plate for the piston. The entire apparatus is made of steel, including fine filters at the top and bottom of the plate to prevent the clay particles from migration. Solution is collected from both the top and bottom of the sample, to shorten the water pathway and decrease the collection time. Table 3 shows the parameters used to extract pore solution from the two blends. For K90, extraction efficiencies were higher than those reported by Cyr et al. (2008) for cement mortars; for Na-bentonite, extraction efficiency was extremely low and longer time periods did not necessarily increase efficiency. It was determined that an improved strategy to collect sufficient solution for analysis was to subject multiple sub-specimens to shorter extractions, then combine the solutions.

Table 3. Pore water extraction parameters and results

Squeezed Material	Extraction Pressure (MPa)	Extraction Duration (h)	Moisture content (%)	Extraction Efficiency (%)
B-8SL	690-1379	5	40	4.2
K90-5SL	690-1000	2	30	56

The pH in the pore solution was tested using a pH micro-electrode because of the low amount of solution recovered, especially for Na-bentonite. Additional analyses of several elements are performed, but not yet available to show in the present study.

Solid samples were also obtained, dried using isopropyl alcohol and subjected to XRD, TGA and NMR analyses. Selected data from TGA that are available to date are shown in this study. For TGA analysis, the cured samples were dried using solvent exchange method (Korpa and Trettin 2006), using isopropyl alcohol as solvent and oven dried afterwards at 80 ^{0}C for 24 hours to drive away the residual solvent. The dried samples were then analyzed using Q600 SDT under argon gas atmosphere. The sample was heated from 5^{0}C to 1000 ^{0}C at 5 ^{0}C/minute rate.

RESULTS AND DISCUSSION

Compaction and 7-day strength tests

The compaction curves for the six material-binder combinations are shown in Figure 2, along with the compaction curves of K90 from Chrysochoou (2014). The two K90 datasets both yield an optimal water content of 32% for PC and a higher OMC for SL (36% in the 2014 study (Chrysochoou 2014), 40% in the current study). K35 with larger particle size and lower plasticity yields both a lower OMC (25% for PC and 30% for SL) and higher maximum dry unit weight. Kavak and Baykal (2012) reported a lower OMC of 25% for a natural kaolinite clay with coarser particle size (42% >75 μm) modified with 4% lime. Bentonite had a flat curve, as expected for this type of mineral, with an OMC around 28% for PC and 30% for SL.

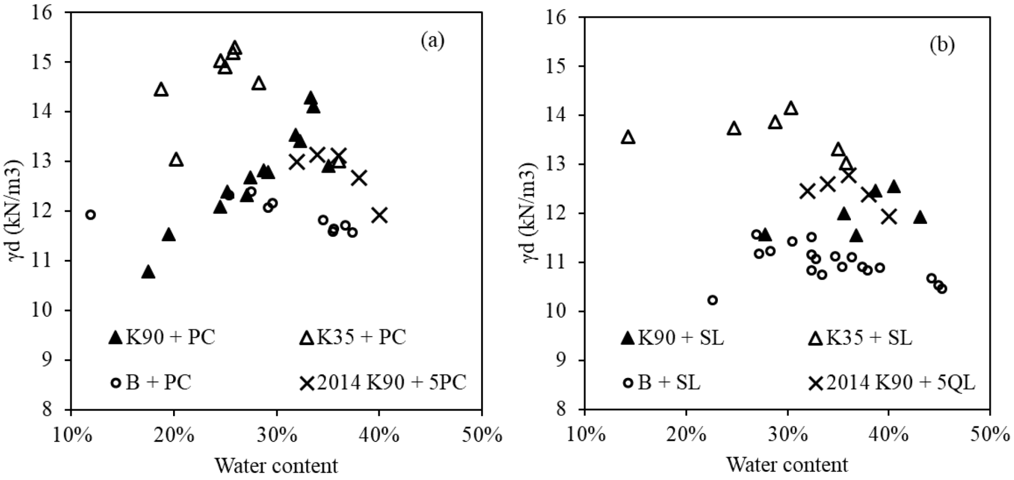

Figure 2. Compaction curves for the three clays mixed with 5% PC (a) and 5% SL (b)

It has long been established that the maximum strength for chemically stabilized clays does not necessarily coincide with the OMC for compaction; for example, Horpibulsuk et al. (2010) observed maximum UCS at 1.2 OWC for a silty clay, which they attributed to the presence of a higher amount of cementitious compounds. Consoli et al. (2009) found little effect of the molding water content in the UCS of lime treated clay. Little (1999) suggested a protocol of testing lime-stabilized samples at three water contents, optimum, 1% above optimum and 1% below optimum.

The results of the UCS tests at 7 days curing and various water contents for the three clays are shown in Figure 3. The maximum UCS at 7 days for Na-bentonite was observed at 38% water content for 5PC and 40% for 5SL, even though the 5SL tests had a lot more scatter, with less clear maximum compared to 5PC. Both of these values are at ~1.35 times the OMC of the respective compaction curve. While the 5SL UCS values showed more scatter, they were clearly higher compared to the 5PC blends. Conversely, both kaolinite materials had higher UCS values for the 5PC blends compared to the 5SL ones. K35 showed maximum UCS at 21% for 5PC and 25% for 5SL, both of which are 0.8 times the OMC. K90 had very similar values in terms of the absolute UCS and the max UCS was at the OMC for 5PC and at 33% (0.8 times the OMC) for 5SL. The maximum UCS achieved was similar for both K35 and K90, around 800 kPa for

Portland cement and 400 kPa for lime. Thus, the short term strength behavior of the two materials is very comparable despite the differences in particle size. It should be noted that the dry unit weights of all samples were compared with the compaction curve and were found in line with the Proctor test results of Figure 2.

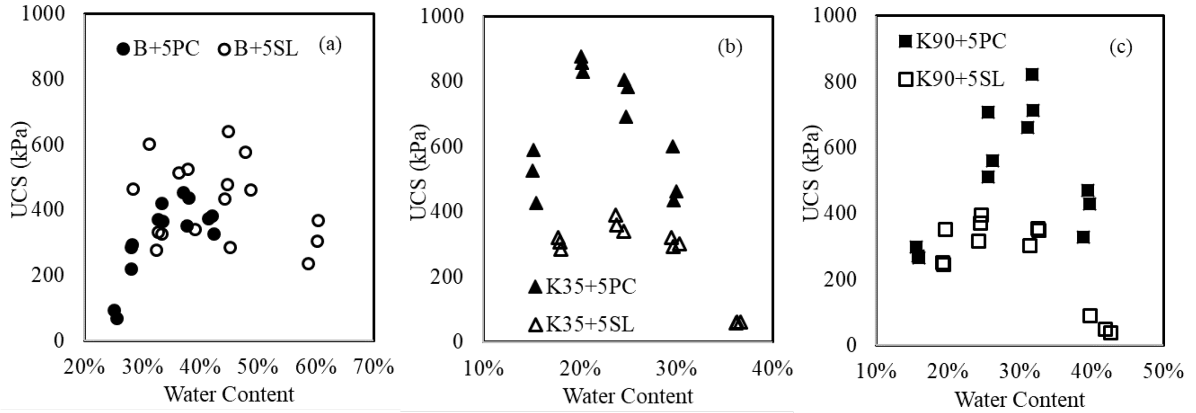

Figure 3. 7-day UCS strength versus water content for Na-bentonite (a), K35 (b) and K90 (c)

In addition to the 5SL samples, Na-bentonite was also treated with 8% lime and tested for 7-days UCS strength, yielding an average of 850 kPa. Given the literature indicating higher optimum levels of lime for smectitic soils and the objective to monitor long term hydration product formation, the long term studies for bentonite were conducted with 8% lime. A water content of 40% was used for all Na-bentonite long term samples based on the results of the 7-day UCS study. Given the similarity in short term UCS behavior of K35 and K90, long term studies were conducted for K90 only, with 5% SL and at a target water content of 30%.

Long-term strength tests

The results of UCS tests up to 180 days of curing are shown in Figure 4. The data for Na-bentonite are consistent with the results reported by Eames and Grid (1960) for pure Wyoming bentonite reacted with 8% hydrated lime. The same authors noted substantial differences in the strength attained for coarser, less plastic Ca-montmorillonite. Similarly, Maubec et al. (2017)

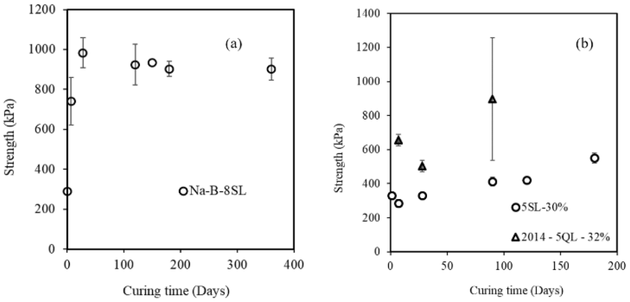

Figure 4. UCS of bentonite treated with 8SL (a) and kaolinite treated with 5SL (b) up to 180 days of curing

reported significantly higher strengths evolving from 500 kPa after one hour of curing to over 1500 kPa at 98 days curing. The bentonite-lime UCS tripled in the first 28 days, followed by no further changes up to 360 days of curing.

Conversely, kaolinite showed continued strength increase from 330 to 550 kPa in 180 days, following an almost linear strength ($R^2=0.93$). The 2014 study (Chrysochoou 2014) had limited data for 32% water content up to 90 days, with substantial scatter, so that comparison is difficult; overall UCS values were higher, with the only difference being the use of 5% quicklime versus slaked lime. Two K90 specimens were prepared with 5% quicklime and the 7-day UCS was ~335 kPa for both, close to the 7-day SL data. The differences are therefore judged to not be statistically significant. Maubec et al. (2017) also studied a kaolinite clay of higher plasticity (PL 40, LL 58) treated with 10% quicklime and reported a modest strength increase from 200 to 400 kPa within one day of curing, followed by no further increase up to 98 days of curing. When the temperature was increased to 50ºC, a quasi-linear trend in strength increase up to 2000 kPa was observed within 98 days.

It is clear from these results that even for relatively pure soils dominated by single minerals, there are several parameters that influence strength development over time; larger particle size is correlated to higher strength; higher plasticity to lower strength. It is also known that different minerals have different reactivity with respect to the formation of cementitious products; montmorillonite is more reactive, releasing more Al and Si into solution, while kaolinite is much less reactive. The temperature experiments of Maubec et al. (2017) confirm that increased reactivity associated with increased temperature can lead to very rapid strength increases that can only be explained by chemical reactions and not by the mechanical properties of the soil.

Two questions arise from this analysis:

a) How can we evaluate soil reactivity over time and the factors that control it?
b) How can we explain differences in reactivity of relatively pure soil minerals from different sources?

Answering the second question requires a robust experimental and theoretical framework to address the first question. In the following sections we will present data of the proposed approach to build this framework.

Pore water extraction results

The evolution of pH in the recovered pore solution for Na-bentonite and K90 is shown in Figure 5. Both solutions start above the equilibrium pH of a saturated lime solution (12.4), 12.7 for kaolinite and 13 for Na-bentonite. Lothenbach et al. (2006) attributes the increase in the cement solution pH to 13 to the need for electroneutrality in solution.

The rapid decrease in pH in Na-bentonite over time can be attributed to the quick consumption of free $Ca(OH)_2$ to form CAH and CSH products. The stability pH for most CAH minerals (hydrogarnet, ettringite if sulfate is present, monocarboaluminate) is generally in the range 10-11; CSH products typically persist to pH 9, with progressive decalcification first through incongruent dissolution down to pH 9.8, then through congruent dissolution (Baston et al. 2012).

The consumption of free lime agrees with the fact that strength remains constant after 28 days. An equilibrium pH of approximately 10 indicates that cementitious products are stable and that CSH likely dominates the hydration products. De Windt et al. (2014) also observed pH decrease for Ca-bentonite treated with 10% lime; at 20ºC, the pH decreased from 13 to 12 within

28 days, then remained steady, while at 50°C, it decreased to 10.5 by 28 days and remained constant up to 98 days. These results agree with this study.

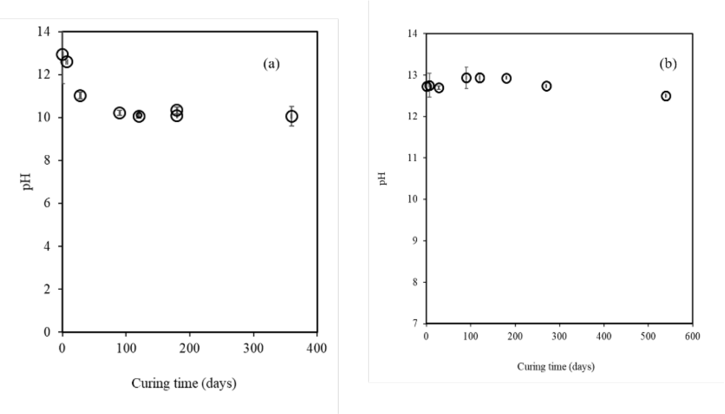

Figure 5. Evolution of pH in pore water over time in Na-bentonite (left) and kaolinite (right).

Conversely, the pH of the K90 blend remained at 12.9 even after 180 days. This is attributed to the lower reactivity of kaolinite, so that release of silica and alumina to form cementitious products is the limiting factor. Free lime remains in solution even up to 180 days of curing, with moderate strength increases.

TGA results

The difference in lime consumption between the two clays, Na-bentonite and kaolinite is also observed from the solid TGA results, as shown in Figure 6. The amount of lime is estimated as the mass loss in the TGA spectrum between the temperatures of 350°C and 400°C. In Na-bentonite the amount of remaining lime drops to half of the initial amount within 7 days whereas in kaolinite the consumption is slower. It should be noted that the required drying of the material results in a partial loss of free Ca(OH)2 prior to the experiment, so that the values reported by TGA are likely an underestimation of the actual free lime content in the sample. Figure 7 shows the amount of formed CSH, estimated from TGA as the mass loss between the temperatures of 100°C and 350°C, compared with the increases in UCS during the same time period. It is evident that the formation of cementitious compound (CSH) is in step with the strength increase for both kaolinite and Na-bentonite.

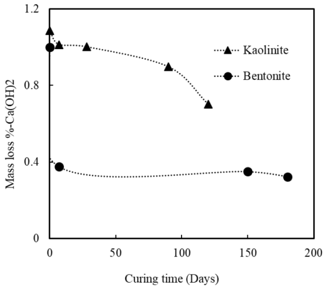

Figure 6. Quantitative TGA analysis on free lime in the system of B-7SL and K90-5SL up to 180 days of curing

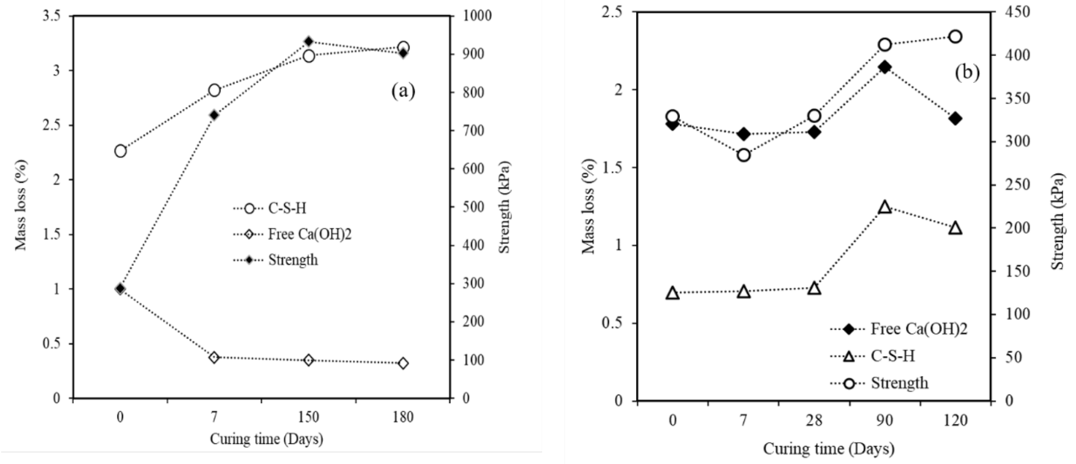

Figure 7. Evolution of portlandite, hydrates weight losses and unconfined compressive strength with time for B-8SL (left) and K90-5SL (right)

CONCLUSION

This study investigates the influence of several parameters on strength development of two clay minerals, Na-bentonite and kaolinite, mixed with lime and Portland cement. The study long-term goal is to develop a kinetic geochemical model that links the chemical reactions in cementitious clay systems with strength evolution.

Particle size of kaolinite was observed to have little influence on the 7-day UCS of specimens treated with 5% slaked lime or 5% Portland cement. A water content slightly dry of optimum was observed to generate the highest UCS values for both particle sizes and binders. Conversely, Na-bentonite yielded higher UCS wet of optimum (1.4 times the OMC) for both cement and lime.

Long term strength tests for the lime blends up to 180-360 days showed that bentonite mixed with 8% slaked lime plateaued at 400 kPa after 28 days of curing. The pore solution extract indicated that pH dropped from 13 to 10 within the same time frame, then remained constant. The TGA analysis confirmed that this trend was associated with a rapid consumption of free lime. Conversely, kaolinite maintained a pH of 13 up to 180 days and free consumption was gradual according to TGA. The strength increased almost linearly with time, and the rate of increase was in step with the apparent rate of CSH formation as estimated by quantitative TGA analysis.

Future work includes full pore solution analysis as well as quantitative analysis of the solid with NMR and XRD to enhance the TGA data. The solid and pore solution data will be combined to obtain a full kinetic quantitative model for the two minerals.

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