

# Influence of Chlorides and Hydroxides of Calcium and Sodium on Consistency Limits of a Fat Clay

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Data are presented to show the relative effects of various quantities of sodium chloride, calcium chloride, sodium hydroxide, and calcium hydroxide on the liquid limit, plastic limit, shrinkage limit, and pH value of a highly plastic fat clay. Values were observed immediately after testing and after periods of 1, 4, and 18 months. The mechanisms by which the additions of salts may influence consistency properties of clays that are discussed include (a) the physical presence of the additive, (b) the effect on surface tension, (c) changes in viscosity in the aqueous phase, (d) promotion of cation exchange, (e) effect of quantities of additive on flocculation and hydration, and (f) effect on soil bacteria. Conclusions drawn from the data compare the essential differences between the results obtained with the different admixtures.

● THIS STUDY was undertaken in connection with research (1) on the effect of lime on the properties of fat clay.

Much has been written about the role of cation exchange in clays with regard to stabilization. Often the stabilizing effect of lime has been attributed to this phenomenon, despite the large quantities of lime (and thus of  $\text{Ca}^{++}$ ) required to bring about the stabilization and apart from the fact that the stabilized soils were largely calcium saturated prior to additions of lime.

The effects of various amounts of the chlorides and hydroxides of calcium and sodium on the consistency limits of a fat soil is determined so as to compare the influence of the cation and pH.

## PROCEDURES

The soil was air dried and pulverized to minus 40. The chemicals (from  $\frac{1}{2}$  to 15 percent by weight) were added in solution with enough water to bring the mixture to a moisture content of 66 percent (the liquid limit of the natural soil). The lime was freshly prepared from  $\text{CaO}$ . The solutions (suspensions in the case of lime) were well mixed in the soil and stored in sealed jars. Tests were run immediately after mixing, after 1 month, after 4 or 6 months, and after 18 or 24 months (without prior air drying).

## THE SOIL PROPERTIES

The soil tested (from the Valley of Jezreel) is well known in Israel, being highly plastic (LL 65-80, PI 43-55, SL 8-10), and exhibits severe swelling properties. The cation exchange capacity is 46.6 me per 100 gm ( $\text{Ca} = 32.6$ ,  $\text{Mg} = 11.7$ ,  $\text{Na} = 1.3$ ,  $\text{K} = 1.0$ ). There is less than  $\frac{1}{2}$  me of soluble salts per 100 gm soil (as determined from a 5:1 extract). The pH of the soil is 7.5. Clay mineral analyses (X-ray diffraction and D.T.A.) revealed that the dominant mineral was dioctahedral smectite and that very little kaolinite was present. The soil is a silty clay that contains 10 percent calcite (of all particle sizes) by weight and 3 percent organic matter. It has a free swell of 110 percent.

## RESULTS AND DISCUSSION

The results are reported in Figures 1 and 2. Among the many mechanisms by which the additions of salts might influence the rheological-consistency properties of clays are the following:

1. The physical presence of the additive thus increasing the effective volume of the soil water by acting as a filler.
2. The effect on surface tension.
3. Changes in viscosity of the aqueous phase.
4. Promoting cation exchange and thus changes in the double layer, hydration and changes in interparticle forces.
5. The effect of larger quantities of electrolyte on the double layer from the point of view of flocculation and hydration.
6. pH and its effect on the double layer, on the clay mineral itself, and on organic matter.
7. Effect on soil bacteria and subsequently on the soil organic matter.
8. Solubility relationships in the soil water.
9. Effect on oriented water.

Because of the complexity of the reactions and the relatively low state of knowledge, it would be very difficult to ascribe with any certainty variations in soil properties as due to any one or more of these factors. However, suggestions as to the nature of the cause of the variations are presented for whatever they may be worth.

## LIQUID LIMIT (LL)

It is evident that additions of NaCl and CaCl<sub>2</sub> affect the soil essentially in a very similar manner, except that the additions of NaCl lower the LL more. The LL expressed on a basis of soil only (that is, discounting the salt) is hardly affected by large additions of CaCl<sub>2</sub>. If one should consider the salt acting as an inert filler in the water, it is evident that the soil interparticle spacings at the liquid limit have not necessarily been altered. If so, it should be expected that NaCl would cause lower LL's than CaCl<sub>2</sub> due to its larger volume both when considered on the basis of equivalent quantities and similar proportions by weight. This is so (more obviously) for the tests run after 18 months.

There appears to be in the case of CaCl<sub>2</sub> a tendency for the LL to decrease until 4 months, after which a reversal takes place that is very probably parallel to the increase in LL of the raw soil. (It is interesting to note that the LL of the raw soil originally 66, rose to 75 within a period of 18 months of storage at a high water content and, as a result of air drying, subsequently fell to 69). The changes with time in the case of NaCl additions are not as regular.

The influence of the alkalis is far more striking. Additions of lime cause the LL (tested immediately after mixing) to drop, the smaller additions being of greater importance. Within a month, the mixtures containing 4 or more percent lime (expressed on the basis of CaO) had hardened and were exuding a gas reminiscent of NH<sub>4</sub> and with an alkali reaction. The LL rose considerably, but the 24 months' determination shows a tendency for a reversal of the trend for the smaller effective additions. The initial decrease in LL may be ascribed partly to the influence of lime acting as an inert material and partly to the influence of high pH on the dispersion and reduction of strength of silicate pastes. The latter has been described by Weyl (2). This is supported by the facts that the significant drop in LL is brought about by up to 4 percent lime (in terms of CaO) and that with further additions a decrease occurs of the order of magnitude of what might be caused by additions of inert material.

The subsequent increase could be ascribed to increased interparticle attraction, but a simpler and probably more correct explanation would be that, as a result of the hardening, the mixtures acquired a new texture. Thus the clay may be regarded as being in the form of small, porous aggregates whose size and number is probably a function of the degree of pulverization of the sample.

Whether the LL of a cemented clay rises or falls is dependent on, among other factors, the arrangement and density of the soil particles at the time of the cementation.

Thus the clay particles that were permitted to harden at a high density will be much less porous than those that have hardened at a low density. The portion of the moisture content at LL that is due to water in the voids of the individual aggregates varies, and so accordingly should the LL. Whether the aggregates cause a decrease or increase depends on the porosity of the aggregates, their size, and the LL of the material in the completely broken-up state.

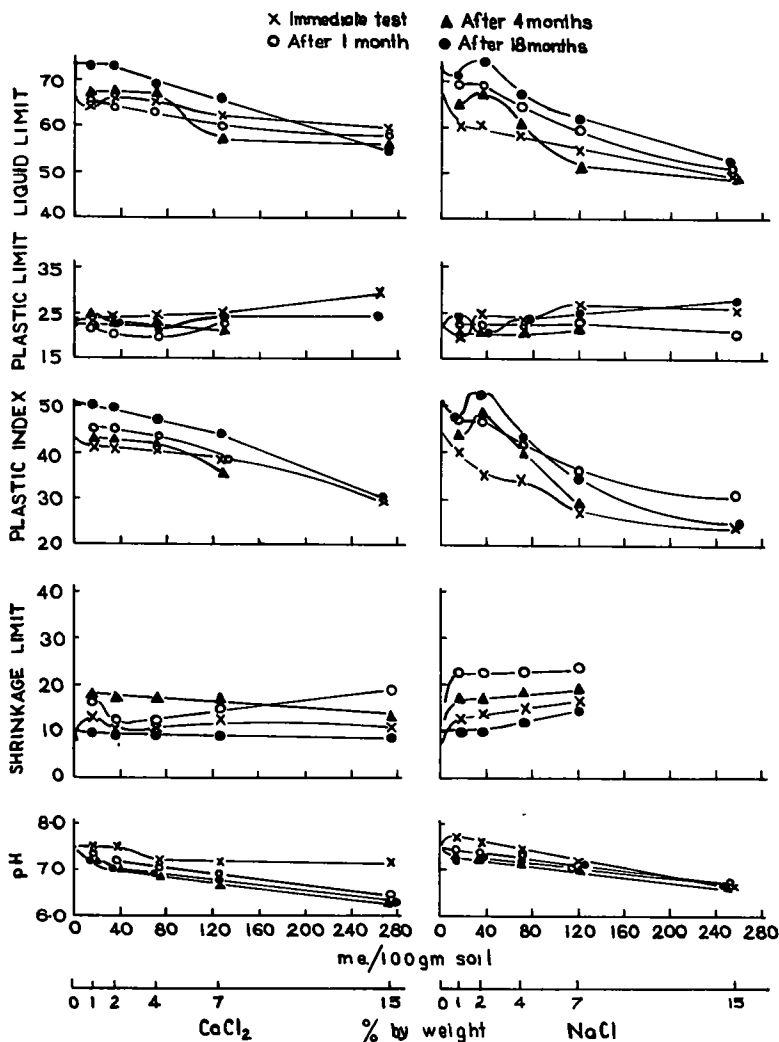


Figure 1. Changes with time in consistency limits, SL, and pH due to additions of  $\text{CaCl}_2$  and  $\text{NaCl}$ .

The mixtures of soil-NaOH stiffened but did not harden and, as in the case of the soil with larger amounts of lime exuded upon addition of the NaOH a gas reminiscent of  $\text{NH}_4$ . The color of the soil darkened considerably and the free liquid (upon placing the soil paste in water) was black. This is probably due at least partially to the destructive reaction of NaOH on the organic matter.

The increase in LL at small additions of NaOH is in keeping with Na being absorbed in the exchange complex. This effect decreases with time, due probably to a strong

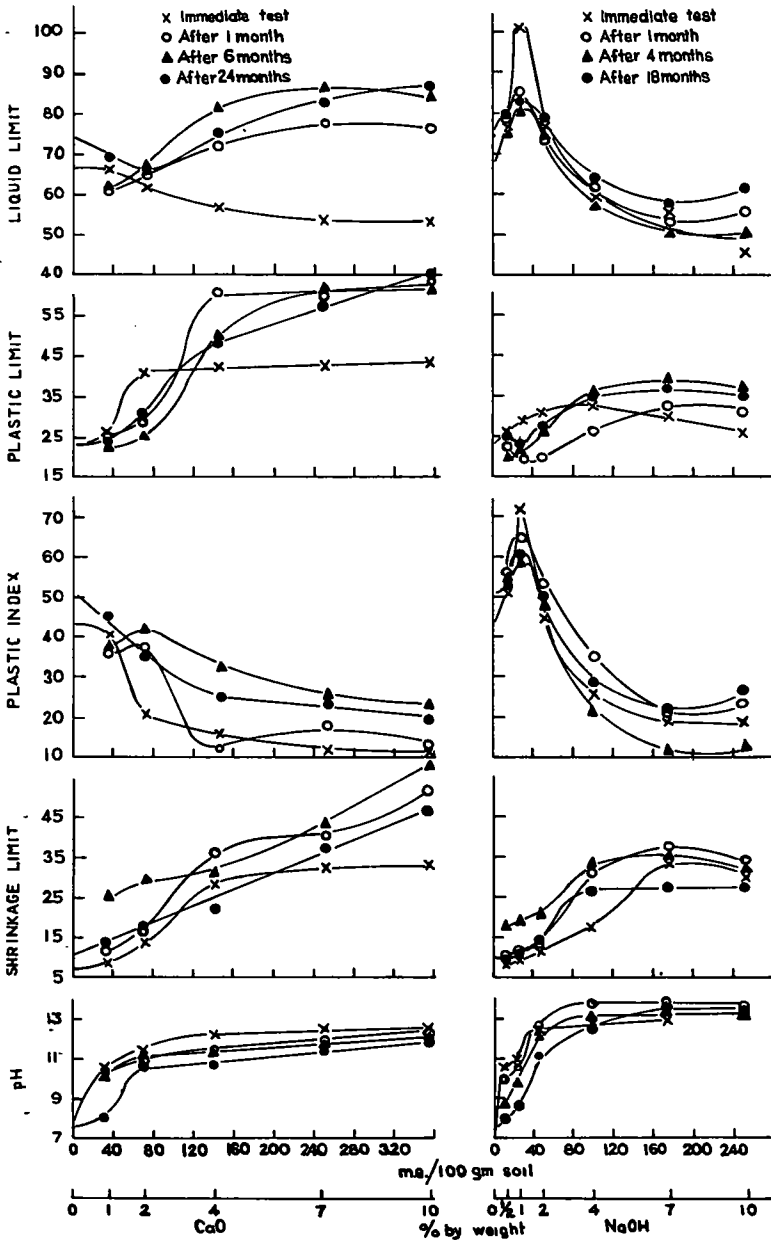


Figure 2. Changes with time in consistency limits, SL, and pH due to additions of CaO and NaOH.

countereffect (of high pH) that at higher quantities of added NaOH tends to reduce the LL. The destruction of humus might tend to increase the LL by causing a decrease in the degree of aggregation. It is not felt that the subsequent release of  $NH_4$  would be important to the exchange complex. The changes with time for the soil with higher NaOH content are irregular.

PLASTIC LIMIT (PL)

The additions of  $CaCl_2$  or  $NaCl$  cause no significant change in the plastic limit. Those small changes that do occur are not conducive to analysis because of the nature

of the test itself. The soil did not become noticeably less sticky or tough as a result of the addition of the chlorides. As opposed to this, the PL was considerably affected by all but the smallest additions of lime. The soil feels and behaves as a silty soil. For the highest addition of lime, the PL tends to rise with time, but for the additions of 2 to 7 percent there occurs (after the initial increase) a drop that tends to decrease after 6 months. The initial increase in PL occurs with the 2 or 7 percent addition of lime (expressed on the basis of CaO) and further increases are of no further significance, indicating perhaps a flocculation. However, the tests after a longer period show the positive effect of amount and an aggregation is indicated.

The smaller additions of NaOH cause a small decrease in the PL such as might be expected to be brought about by medium entering the exchange complex. This apparently requires some time since the initial effect is in the opposite direction. Larger additions of NaOH cause the PL to rise rapidly. The PL does not change significantly after 4 months. The effect of NaOH is consistent with an aggregation that is however smaller than in the case of lime additions.

### PLASTIC INDEX (PI)

The influence of the additives on PI is presented in Figures 1 and 2. It is not thought justified to enter into a detailed discussion of the changes that occur, since the salt concentration at LL and PL are quite different and thus changes that are influenced by electrolyte concentration do not occur at the same salt content expressed in terms of dry soil. The PI is not in itself a specific independent property, but it is interesting to note that for all additions of NaCl or CaCl<sub>2</sub> the soil remains (on the plasticity chart used in the Casagrande soil classification) a CH soil. However, the larger additions of NaOH and lime cause the soil to cross the A-line on the plasticity chart and would, on its basis for classification, be termed a MH or OH (Fig. 3).

Terzaghi (3) ascribed the properties of a halloysite clay that falls in the same region below the A-line to the "simple assumption that most of the clay fraction of the soil occurs in the form of clusters or hard porous grains with rough surfaces, each of which consists of a number of firmly interconnected clay mineral particles." This might very well be applicable in the case of some of the soil-lime mixtures (which obviously hardened) and in the case of some of the soil-NaOH mixtures.

### SHRINKAGE LIMIT (SL)

In general the addition of chlorides tends to produce an increase in the SL, which is effected mainly by the smallest addition, further additions being of little influence. With additions of both NaCl and CaCl<sub>2</sub>, the SL rises initially and then tends to drop. The large variations that occur during aging of the mixtures are of considerable interest and it might be said quite unanticipated. It is not very likely that the large amounts of chlorides were rendered insoluble or absorbed. The appearance of a green slime in the jars of some soil-CaCl<sub>2</sub> and NaCl mixtures leads to the thought that the addition of the salts, and particularly of the calcium salt, promoted the activity of soil microbes that effected changes in the organic matter. Thus the soil reverted to a more dispersed state.

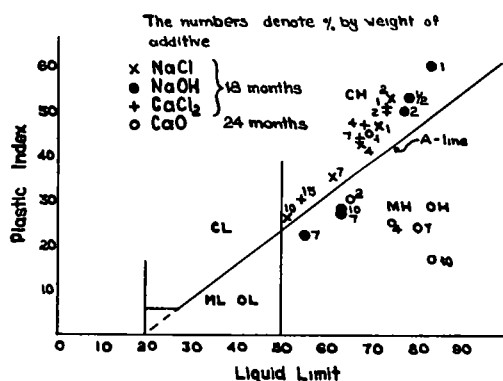


Figure 3. Plot of soil-chlorides and alkalis mixtures on plasticity chart.

Winterkorn (4) has pointed out, in relation to cohesive soil stabilization and the effect of soil microbes, that "in fact, with time some of the stabilized soils become less stable than the untreated natural soils." There exists the interesting possibility of pro-

moting and utilizing this phenomenon where an increase in soil dispersion is required, such as in impermeable earth blankets for water ponds.

There is a general tendency for the addition of the hydroxides to cause an increase in the SL within a certain period of time. After that time a drop occurs relatively more significant for the smaller additions of the hydroxides. These results are consistent with a change in aggregation or texture, and changed interface properties are probably also of importance. A countereffect or partial neutralization is indicated by the tendency of the SL to drop after a period of time.

The effect of additions of NaCl and CaCl<sub>2</sub> on the pH are very similar except that immediately after addition, the smallest quantities of NaCl cause a slight rise that does not occur in the case of CaCl<sub>2</sub>. Otherwise, additions of these salts generally cause a progressive decrease in pH. The additions of both lime and NaOH cause an increase of pH to that of the pH of a saturated aqueous solution. The pH subsequently drops, more so for the mixtures with smaller additions of hydroxides. The higher pH readings for NaOH should be treated with caution due to the difficulty of true pH determination of solution with such high concentration of Na<sup>+</sup> at high pH.

The large amounts of lime required to bring the pH of the soil slurry to 12.6 is remarkable. The concentration of lime is about 8 gm per 100 gm water whereas the solubility in water is less than 0.1 gm per 100 gm water. This rapid "absorption" of the lime might very well not be necessarily dependent on prior solution. It is interesting to note that the findings of Clare and Cruchley (5) with regard to changes in pH with time (based, of course, on the initial pH determinations) can be related to the amount of lime absorbed. If this be really so, it would appear that more lime is "absorbed" with time for the richer lime-soil mixtures.

#### CRITIQUE

It is felt, in retrospect that a program of the nature described is of a limited value that by itself does not give as conclusive an answer as might be desired. While it is true that the Atterberg Limits and the corresponding Plasticity Chart are of considerable local value for purposes of comparison and classification, it is felt that an excessive reliance has been placed on them in spheres in which they are less applicable. The over-faithful use of the PI concept has tended to obscure the need for a more precise classification.

The PI does not necessarily reflect the mechanical properties of the soil. A stiff, non-slaking clay or shale may be described as CH and a lime-stabilized clay, or for that matter any cemented or aggregated clay, might be described as OH or MH, etc. The classification based on the plasticity properties of the ground soil is of very doubtful value. It is no reflection of compressibility or swelling and certainly does not reveal the high water stability of the clay nor its strength. The texture is to an important extent a function of the degree of pulverization, and so accordingly are the consistency limits. It is therefore felt that to anticipate the engineering behavior of soil materials on the basis of their consistency properties alone might very well lead to the neglect of otherwise suitable materials.

#### CONCLUSIONS

1. There is no essential difference between the influence of NaCl and CaCl<sub>2</sub> in the range of quantities added to the consistency properties of the soil. Neither of these salts causes any significant alteration that remains for the duration of the period of testing.
2. The hydroxides have a similar influence on the soil except for a difference in effect on LL. This is (at higher concentration of NaOH) probably a reflection of the weaker cementation that occurs at this high moisture content (and low density). This is reflected in the smaller changes effected by NaOH in PL and SL.
3. The essential difference between the influence of the hydroxides and the chlorides is in the relatively high increases in SL and PL that the former cause. These increase with higher hydroxide content and accordingly with increase in pH.

4. In all probability, the degree of "stabilization" of a soil is most likely to be reflected by changes (increases) in the PL (and to a lesser degree in SL). (It has been previously reported (1) that additions of the chlorides to this soil did not impart further strength nor resistance to slaking, whereas the addition of equivalent amounts of the hydroxides did.)

5. Large variations with time occur and reactions should be checked over an extended period of time.

6. In order to minimize the influence of changes in the soil due only to rewetting, it is felt that soils should be wetted well in advance of the commencement of research programs.

#### ACKNOWLEDGMENT

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