# The causes and effects of aging in quick clays

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The physicochemical properties of a clay from La Baie, Quebec were found to be typical of Champlain quick clays: very low plasticity, liquidity index greater than 3, sensitivity greater than 500, and pH of about 9.5. The mineralogy is characterized by the abundance of primary or "rock flour" minerals such as feldspar, quartz, amphibole, and calcite, with illite as the principal clay mineral. The pore water chemistry consists predominantly of sodium bicarbonate. Low concentrations of sulfate, calcium, and magnesium and high alkalinity and pH are attributed, in part, to anaerobic sulfate-reduction processes taking place *in situ*.

Quick clay samples stored in the laboratory showed signs of aging regardless of the storage procedure. The remoulded strength and the liquid limit increased with time, whereas the sensitivity, the liquidity index, and the pH decreased. The water content, plastic limit, and undisturbed strength remained practically unchanged. The pore water concentrations of calcium, magnesium, and sulfate increased by severalfold.

The aging phenomenon is attributed, for the most part, to the oxidation of iron sulfide, which results in the formation of iron hydroxide and sulfuric acid. The production of acid causes the dissolution of calcium carbonate, which increases the concentration of divalent cation in the clay, thereby reducing interparticle repulsion and increasing the remoulded strength. The oxidation of organic matter, resulting in the formation of carbonic acid, also contributes to the aging by its effect on the solubility of calcium carbonate.

*Key words:* aging, chemical reactions, physicochemical phenomena, sensitivity, time effects.

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Il a été constaté que les propriétés physico-chimiques d'une argile de La Baie, Québec étaient typiques des argiles sensibles Champlain: très faible plasticité, indice de liquidité supérieure à 3, sensibilité supérieure à 500 et pH d'environ 9,5. La minéralogie est caractérisée par l'abondance de "poussière de roche" ou de minéraux primaires tels que le feldspath, le quartz, les amphiboles et la calcite. L'illite représente le principal minéral argileux. La chimie de l'eau interstitielle est constituée principalement de bicarbonate de sodium. Les faibles concentrations de sulfate, de calcium et de magnésium, de même que la forte alcalinité et la valeur élevée du pH sont attribuées, en partie, aux processus de réduction anaérobique du sulfate qui se produit *in situ*.

Des échantillons d'argile sensible entreposés en laboratoire ont montré des signes de vieillisement indépendamment de la procédure d'entreposage. La résistance remaniée et la limite liquid ont augmenté avec le temps alors que la sensibilité, l'indice de liquidité et le pH diminuaient. La teneur en eau, la limite plastique et la résistance intacte sont demeurées à peu près inchangées. Les concentrations de calcium, de magnésium et de sulfate dans l'eau interstitielle ont augmenté drastiquement.

Le phénomène de vieillissement est attribué, en grande partie, à l'oxydation du sulfure de fer qui résulte en la formation d'hydroxide de fer et d'acide sulfurique. La production d'acide cause la dissolution du carbonate de calcium, et augmente la concentration de cations bivalents dans l'argile, réduisant ainsi la répulsion inter-particule et augmentant la résistance remaniée. L'oxydation de matière organique, résultant en la formation d'acide carbonique, contribue aussi au vieillissement par suite de son effet sur la solubilité du carbonate de calcium.

*Mots clés:* vieillissement, réactions chimiques, phénomènes physico-chimiques, sensibilité, effet du temps.

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## Introduction

Soil engineering studies often include laboratory tests aimed at predicting the behaviour of the *in situ* soil. Generally, undisturbed samples are taken from the site and transported to the laboratory, where they are stored at room temperature and 100% relative humidity to prevent water losses. Whether the properties measured by laboratory tests carried out weeks to months after sampling are representative of the *in situ* characteristics of the soil is questionable. Many cases have been reported where significant changes in sensitivity, Atterberg limits, and pore water chemistry occurred during storage. The process responsible for these changes, generally referred to as aging, has been observed in Scandinavian as well as Canadian clays.

Bjerrum and Rosenqvist (1956) observed an increase in the Atterberg limits of a marine clay from Asrum, Norway, that was a result of aging. The plasticity index of a sample rose from 21% to 27% over a 2 year period and was accompanied by an increase in potassium ion concentration in the pore water, which was attributed to the weathering of the clay minerals.

Samples of Swedish clays taken from the Gota River valley lost their original quickness after being stored for 2–4 years. Similar sensitivity reduction was observed *in situ*, as a clay sampled in 1967 at a depth of 1 m below an exposed slide bottom of the 1960 slide at Veston had lost its quickness in the meantime (Söderblom 1969). Quantitative analyses by standard paper chromatography showed that before aging, the quick clay contained mainly $Na^+$ and $SO_4^{2-}$ in its pore water. After aging, there was a significant amount of $Mg^{2+}$ and $Ca^{2+}$ and a marked increase of $SO_4^{2-}$ (Söderblom 1974). According to Söderblom (1969), "the change from anaerobic to aerobic state and the accompanying changes in the microbial activity may be the most important factor in the aging process."

Torrance (1976) reported the effects, on the pore water chemistry, of 3 months' storage under a wide variety of standard and modified storage procedures. The material was a soft Champlain clay with a low salinity and a sensitivity of 10–20. Irrespective of the storage method, the salinity and the percentage of divalent cations in the pore water had increased. The most

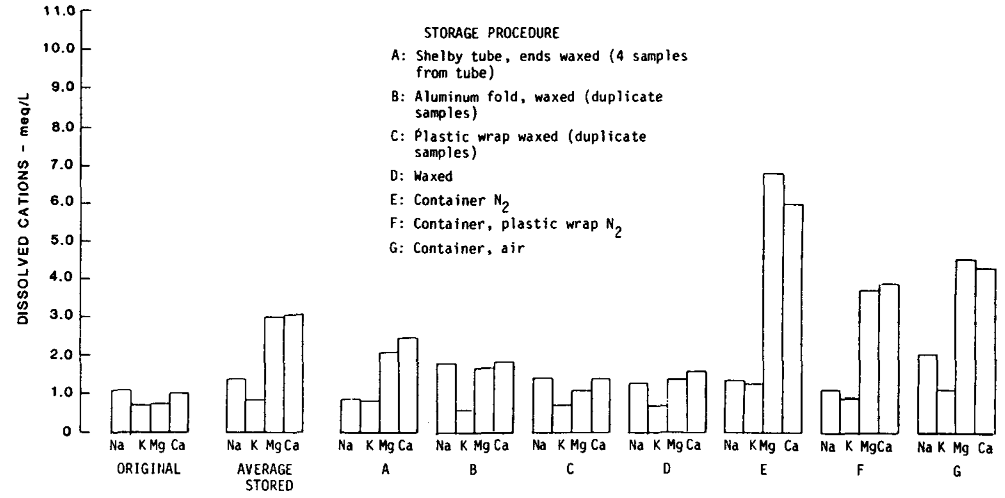


FIG. 1. Effect of 3 months' storage upon the cation distribution in the pore water under various storage procedures (adapted from Torrance 1976).

conspicuous changes were observed for the clay stored in plastic containers without the protective seal of the wax (Fig. 1). According to Torrance, the increase in the concentration of calcium and magnesium in the pore water during aging is probably related to attack on carbonates present in the soil.

In order to better understand the geotechnical and chemical changes occurring in a quick clay during storage, an extensive testing program was carried out on a Champlain quick clay from La Baie, Quebec. After measuring the initial characteristics of the material, samples were stored and tested periodically over a period of 1 year to evaluate the effect of various storage conditions. The main results of the testing program are presented in this paper. Their interpretation and significance in geotechnical practice are emphasized.

## Sampling

The quick clay samples used in the testing program were obtained from La Baie near the Saguenay River in the Province of Quebec. The clay now covering most of the Saguenay – Lac Saint-Jean area was desposited in the LaFlamme Sea, an extension of the Champlain Sea, after the last glaciation some 10 000 years ago. The sampling site is located about 20 km from Saint-Jean-Vianney where the largest landslide known to have occurred in the Champlain clay took place some 400–500 years ago and involved 20 $km^2$ of land, displacing an estimated volume of $200 \times 10^6$ $m^3$ of soil. In 1971, a flow slide occurred in the same crater, causing the loss of 31 lives and carrying 40 houses to destruction (Tavenas *et al.* 1971).

The samples were recovered in October 1979 using 76 mm diameter Shelby tubes. Within 1 week after sampling, the clay was extruded from the sampling tube. The sample surface that had been in contact with the steel tube was removed by scraping, in order to avoid any potential contamination by metallic ions. The clay was then cut horizontally in 10 cm long samples, which were waxed with several thin layers of paraffin. In order to monitor any change in properties that occurred during transport from La Baie, Quebec to Berkeley, California, some samples were tested immediately after the extrusion of the clay from the tube. Attenberg limits were determined following standard procedures and without predrying the soil. Undisturbed and remoulded strengths were measured by means of the Swedish fall-cone test.

## Experimental methods and material characteristics

Upon reception of the samples in the laboratory, about 1 month after sampling, an extensive analysis of the geotechnical and physicochemical properties of the quick clay was undertaken. The purposes of the analysis were firstly to evaluate whether any change had occurred in the geotechnical properties of the material since sampling and secondly to establish the *in situ* or "initial" geochemical characteristics of the clay, which were to be used as a reference to assess the various effects of aging.

### *Material description*

The soil material is an extremely quick, banded silty clay of medium to stiff consistency. Its colour varies from light to dark bluish gray with a few brownish bands. Most of the bands are horizontal but some are inclined by as much as 45° from the horizontal. Their thicknesses range from less than 1 cm to about 30 cm. Pockets and lenses of fine to medium sand are encountered randomly throughout the strata. It is important to note that the bands do not necessarily reflect large differences in grain size and mineralogy, as is the case for freshwater varved clays, which usually show an alternation of horizontal layers of silt and clay. In the case of the La Baie clay, the darker bands are probably related to the presence of metastable iron sulfide.

### *Water content and Atterberg limits*

The distribution of water content with depth (Fig. 2) is typical of the heterogenity of Champlain clays. Variation in water content of as much as 10% may occur within a distance of a few centimetres, but the general trend shows little variation with depth. Most values fall between 40% and 50%.

The Atterberg limits measured 1 month after sampling did not differ significantly from those measured within 1 week of sampling. The plastic limit varies between 16% and 23%, with an average value of 19% and the liquid limit ranges from 20% to 33%, with an average of 25%. The plasticity index is very low with values ranging from 4% to 10%, averaging 6%. The liquidity index varies from 3 to 7 and reflects the extreme quickness of the clay.

### *Stength and sensitivity*

The undisturbed strength, determined by means of the fall-cone test, represents the average of five measurements.

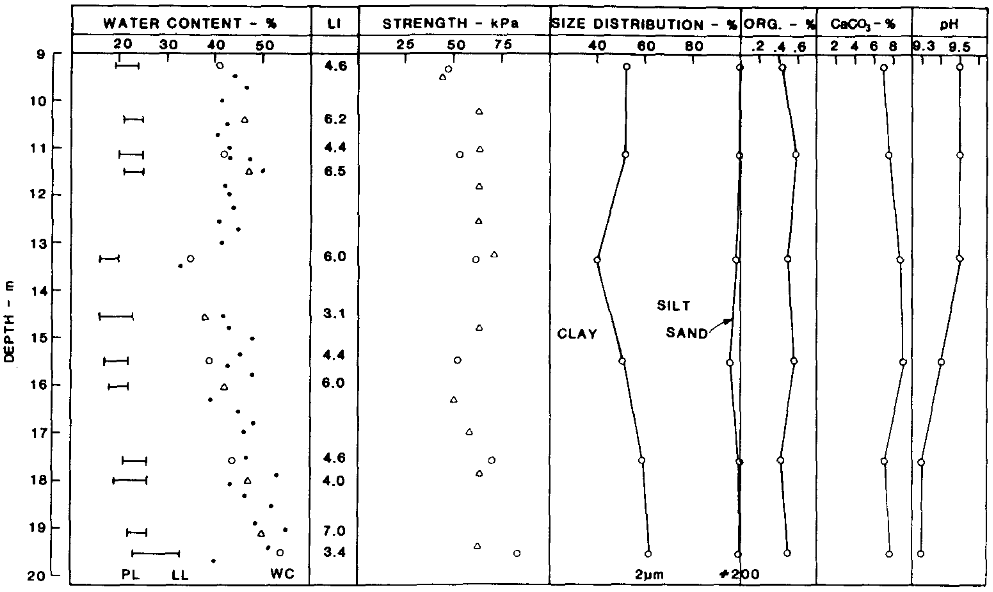


FIG. 2. Geotechnical and compositional characteristics of La Baie clay measured 1 week (△) and 1 month (○) after sampling.

Most values fall between 50 and 70 kPa with a very slight increase with depth. The undisturbed strength measured at 1 month is essentially the same as at 1 week after sampling.

The remoulded strength was determined by the fall-cone test from at least five measurements. Before each test, the soil was thoroughly remoulded in order to minimize thixotropic effects. The test was repeated until a constant reading was obtained, thus indicating a complete remoulding and homogenization of the material. For all the tests performed, the clay samples became so liquid upon remoulding that the penetration of the 10 g cone was greater than 20 mm, which corresponds to a remoulded strength lower than 0.07 kPa and a sensitivity greater than 500.

### *Specific gravity and grain-size distribution*

The specific gravity of the soil solids measured on six samples varied only from 2.75 to 2.78, which reflects a homogeneous mineralogical composition of the material.

The results of grain-size analyses performed on six samples are shown in Fig. 2. The clay-size fraction (−2 µm) varies from 40% to 62%, with the smaller values at mid-depth. Not surprisingly, the grain-size distribution correlates well with the water content of the material and plastic limit profile.

### *Organic matter*

The organic matter content of the clay was measured by redox titration (Rankin 1970). The method is based on the oxidation of carbon by potassium dichromate. The procedure consists of adding concentrated sulfuric acid and a known amount of potassium dichromate to 5.0 g of dry soil. The amount of dichromate that does not react with the oxidizable carbon is determined by titration.

The results showed no particular trend with depth. The organic matter content varied between 0.4% and 0.6%, with an average of 0.5%, which corresponds to 0.3% of oxidizable carbon.

### *Carbonate*

The total insoluble carbonate content was determined using the rapid titration method (Hesse 1971). The procedure consists of adding 50 mL of 1 *N* HCl to 5 g of air-dried soil. The amount of acid that is left after reaction with the carbonate is determined by NaOH titration.

The tests indicated carbonate contents varying between 7% and 9%, with an average value of 8%. No particular trend with depth was observed. Such high values of carbonate content are common for the LaFlamme Sea clays.

### *Soil pH*

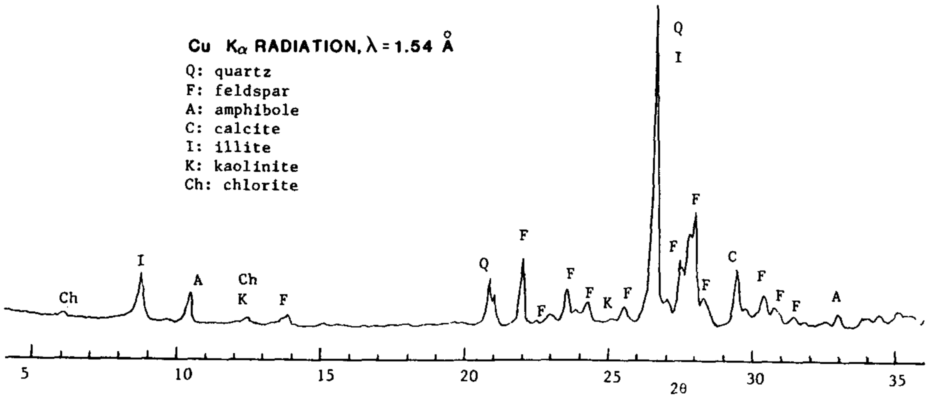
The soil pH was measured in a 1:1 (by weight) mixture of soil and distilled water. Five grams (dry weight) of wet soil of known water content was used for the test. Distilled water was added to the soil to obtain a total weight of 10 g. The slurry was mixed thoroughly and then allowed to stand undisturbed for 1 h, after which the pH was measured by means of a combination electrode and a Beckman pH-meter positioned in near-contact with the bottom of the container. Typically, the reading decreased rapidly to reach a stable value within 2–3 min.

The soil pH measured in the clay samples decreases with depth, with values ranging from 9.6 in the upper part of the boring to 9.3 in the lower part.

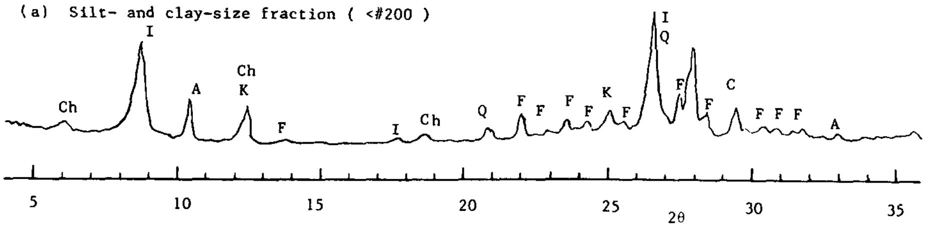
### *Mineralogy*

The mineralogical analysis of the clay was performed by the X-ray diffraction method using a RIGAKU diffractometer and Cu $K_\alpha$ radiation. Six samples from various depths were air-dried and reduced to powder. The material passing the #200 mesh sieve was packed into the sample holder and the surface struck off smooth and level. The X-ray patterns obtained for the six powder samples indicate that the mineralogical composition of the material is virtually the same throughout the profile. As shown in Fig. 3*a*, the material contains a substantial amount of rock flour minerals such as quartz, feldspar, amphibole, and calcite. Illite is the main phyllosilicate mineral. Chlorite and kaolinite are also present in traces.

A semiquantitative X-ray analysis was performed on one sample. Approximately 20 g of air-dried soil was ground for 2 min in a rotative grinder. The powder obtained was packed in the sample holder, smoothed off, and pressed with fine-grained sandpaper to minimize the preferential orientation of platy mica



(a) Silt- and clay-size fraction ( <#200 )



(b) Clay-size fraction ( <2μm )

FIG. 3. X-ray diffraction powder patterns of fraction passing #200 sieve (*a*) and oriented <2 μm fraction (*b*) of sample from La Baie.

and amphiboles (Foscal-Mella 1976). Reference standard minerals were prepared following the same procedure as for the clay. Biotite was used to estimate the illite content, since the two have similar structures. The percentages of the various minerals in the clay were estimated by comparing the intensity of characteristic peaks with the peak intensity of standard minerals. The results are presented in Table 1.

The mineralogy of the clay-size fraction was examined by running an X-ray analysis on samples made of the −2 μm clay suspension allowed to air-dry slowly on glass slides for at least 24 h. The X-ray diffraction pattern of an oriented air-dried sample of the clay-size material is shown in Fig. 3*b*. As expected, the proportion of phyllosilicate minerals is more important in the clay-size fraction. Rock flour minerals, however, remain present in significant quantities. On the pattern of a heat-treated sample (500°C), the peaks at 7 Å and 3.5 Å had disappeared, thus confirming the presence of a small amount of kaolinite which becomes amorphous at 500°C. The oriented and glycolated samples showed no trace of montmorillonite or other smectites.

*Pore water chemistry*

The pore water used for the soluble salt determination was obtained by squeezing the soil in a modified consolidation apparatus. The upper porous stone was covered with plastic and the lower porous stone was replaced by a perforated plastic disc. The water was collected from the base of the sample. A slow loading rate had to be used at the beginning of consolidation to avoid the squeezing out of liquefied soil between the piston and the consolidation ring. Overnight, about 6–10 g of water could be obtained from the squeezing of some 80 g of clay at its initial water content. The ion concentration in the squeezed pore water was not found to be pressure dependent for the range of consolidation pressure used.

The concentrations of various ions were determined using standard procedures. Dissolved sodium, potassium, magnesium, and calcium were measured by atomic absorption spectrophotometry. Sulfate was determined by the turbidimetric method whereby the sulfate ion is precipitated with barium chloride to form barium sulfate crystals. Chloride was measured by potentiometry, i.e. by means of a chloride-sensing electrode coupled with a reference electrode and a pH-meter. The bicarbonate ion was determined by potentiometric alkalinity titration with 0.01 *N* HCl. In all the pore water samples tested, the concentration of $CO_3^{2-}$ was small (less than 5% of the total alkalinity) and, therefore, its value was included in the concentration of $HCO_3^-$. All the above tests, with the exception of the chloride analysis, have an accuracy better than ±5%. For the potentiometric measurement of chloride, the accuracy is about ±10%.

The results of the pore water chemistry analyses are shown in Fig. 4. Sodium and bicarbonate are the predominant species in the pore water of La Baie clay. Their concentrations generally increase with depth. In all the samples examined, the chloride concentration was less than 0.5 meq/L, with no particular trend with depth. The concentrations of dissolved potassium, magnesium, and calcium are also very low, showing a slight increase with depth.

TABLE 1. Mineralogical composition of La Baie quick clay

| Mineral | % by weight |
|---|---|
| Primary minerals | |
| Plagioclase | 45 |
| K-feldspar | 12 |
| Quartz | 13 |
| Amphibole | 10 |
| Calcite | 8 |
| Clay minerals | |
| Illite | 10 |
| Chlorite | 1 |
| Kaolinite | 1 |

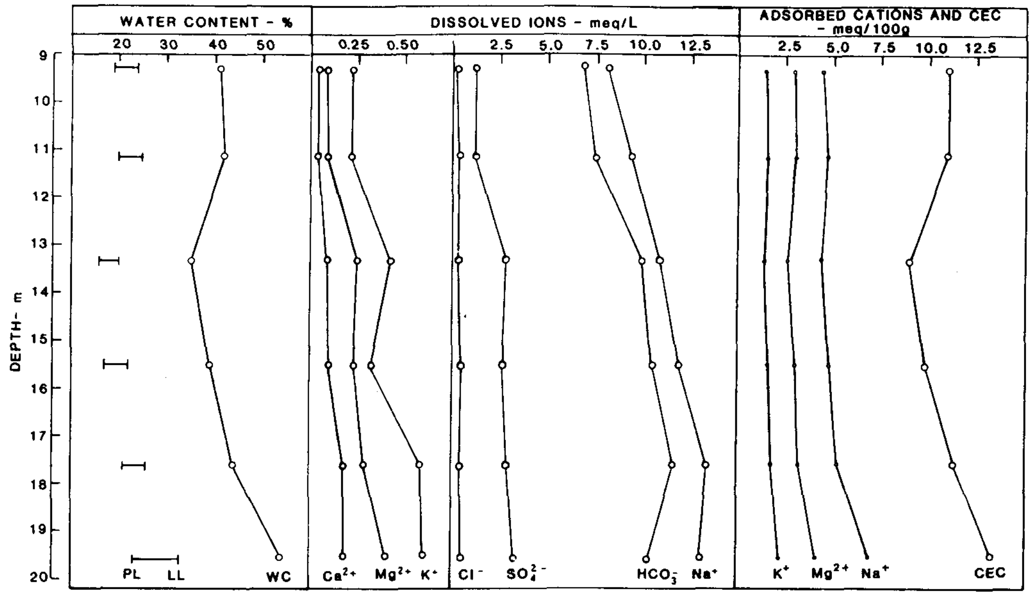


FIG. 4. Pore water and adsorbed layer characteristics of La Baie clay measured 1 month after sampling.

The pore water chemistry analysis shows evidence of leaching and sulfate reduction, two conditions apparently necessary to the development of quickness. The composition of the clay pore water is compared with the average composition of seawater in Table 2. Assuming a depositional salinity of 35 g/L, the concentrations of all ions have decreased since the deposition of the clay, with the exception of bicarbonate, which increased by a factor of 4 because of bacterial oxidation of organic matter. The chloride concentration has been reduced by a factor of 1800, which is indicative of the extensive leaching of the material.

The drastic depletion of calcium and magnesium is believed to be due to precipitation as magnesium–calcite taking place in the sulfate-reduction process, which also causes a decrease in sulfate concentrations and an increase in bicarbonate concentration and pH. The existence of sulfate reduction in a Champlain quick clay was well demonstrated by Donovan and Lajoie (1979). In the absence of oxygen, dissolved sulfates, as well as ferric oxides, are reduced by the bacterially catalyzed decomposition of organic matter. This leads to the formation of metastable iron monosulfide and ultimately pyrite, which is responsible for the black mottles commonly found in quick clays. The chemical equilibria and reactions involved in the process are described in more detail by Lessard (1981).

### *Cation exchange capacity*

The cation exchange capacity, CEC, expressed as meq/100 g of dry soil, was determined by saturating the exchange complex of the clay with $Na^+$, removing the excess $Na^+$ by washing with ethyl alcohol, and replacing the adsorbed $Na^+$ with $NH_4^+$ at pH 7.0. The concentration of $Na^+$ introduced into the ammonium solution was then determined by atomic absorption spectrophotometry. Five grams (dry weight) of soil that had not been predried was used for the analysis.

The CEC measured for six samples varied from 9 to 13 meq/100 g, with an average of 11 meq/100 g, which is typical of the Champlain Sea quick clay. As shown in Fig. 4, the relation of the CEC to depth follows the same trend as the water content and the percentage of particles smaller than 2 μm, which is expected, since smaller particles are associated with higher specific surface areas, higher CEC, and higher water content under a given effective stress.

TABLE 2. Comparison between the composition of seawater and the composition of the pore water of the La Baie clay

| | Seawater* | | Pore water | | Ratio |
|---|---|---|---|---|---|
| Ion | meq/L | % | meq/L | % | seawater/ pore water |
| $Na^+$ | 459 | 77 | 11 | 95 | 42 |
| $K^+$ | 10 | 1.7 | 0.3 | 2.6 | 33 |
| $Mg^{2+}$ | 106 | 18 | 0.2 | 1.7 | 530 |
| $Ca^{2+}$ | 20 | 3.4 | 0.1 | 0.9 | 200 |
| $Cl^-$ | 535 | 90 | 0.3 | 2.6 | 1800 |
| $SO_4^{2-}$ | 55 | 9.3 | 2.0 | 17 | 27 |
| $HCO_3^-$ | 2.3 | 0.4 | 9.3 | 80 | 0.25 |

*Values taken from Sverdrup *et al.* (1942).

### *Exchangeable cations*

The exchangeable cation analysis is carried out by first removing the excess salt dissolved in the pore fluid by washing with ethyl alcohol. The naturally adsorbed cations are then exchanged for $NH_4^+$ by successive washing of the clay with a solution of 1 *N* ammonium acetate at pH 7. The concentrations of the various cations introduced into the ammonium solution by replacement are then determined by atomic absorption spectrophotometry. Ammonium is used as the replacing ion, because the $NH_4^+$ ion is not commonly found in natural soils. Five grams (dry weight) of wet soil was used for the anlaysis. One weakness of the method is that it may lead to an overestimation of the adsorbed calcium as $CaCO_3$ is dissolved. In the case of the quick clay from La Baie, the pH of the soil was lowered from about 9.5 to a value of 7.0 by the addition of ammonium acetate. As the pH decreases, the solubility of $CaCO_3$ is increased severalfold.

The test procedure used in the present analysis yielded values of about 30 meq/100 g for the "adsorbed" calcium. These values are much higher than the CEC and are obviously not representative of the actual amount of calcium present in the double layer of the natural clay. The distributions of adsorbed sodium, potassium, and magnesium with depth follow the same trend as the variation of the CEC (Fig. 4). Sodium makes up nearly 50% of the exchangeable cations, and potassium about 16%. The concentration of adsorbed magnesium, which makes up about 30% of the total exchangeable cations, is very high compared with the amount of magnesium in the free pore water. Although the double-layer theory predicts a larger proportion of divalent cations in the adsorbed system than in the equilibrium solution, it is probable that at least a portion of the measured adsorbed magnesium came from the dissolution of magnesium-calcite.

## Storage procedures

Upon reception, the samples, which had been waxed with several layers of paraffin, were stored in a wet room at 20°C and 100% relative humidity. This represents the storage procedure most frequently used in soil laboratories. For that reason it will be referred to as "standard" procedure. Two months after sampling, several samples were removed from the wet room and stored under "special" storage conditions.

In order to better understand the role of oxidation in the aging phenomenon, several samples were unwaxed and stored at 20°C in airtight plastic containers. This type of storage might be used for sample trimmings or with material after other tests have been performed. These samples are often used for Atterberg limit tests. A total of twelve 400 g samples were placed in three sealed containers filled with air, nitrogen, and oxygen. The nitrogen and oxygen atmospheres were obtained by flushing the container with the appropriate gas for about 5 min. The degree of oxygen depletion was not assessed. A bottle of water was placed in each of the containers to maintain 100% relative humidity.

In order to study the effect of temperature on aging, six 200 g samples were stored at 4°C. After 3 months of storage, the wax on two of the samples was removed, in order to accelerate the rate of aging.

In an attempt to measure the influence of bacterial activity on aging, four 400 g samples were sterilized using X-rays from a $^{60}$Co source. The waxed undisturbed samples were irradiated for 24 h, receiving a total dose of 0.2 MGy (20 Mrad).[1] A dose of 0.02–0.04 MGy (2–4 Mrad) is generally recommended for 100% sterilization (McLaren *et al.* 1957, 1962; McLaren 1969). The effect of irradiation on the geotechnical and chemical properties of the clay is minimal. A visual examination of one sample immediately after sterilization showed the same extreme quickness as before. The sterilized samples were stored in standard conditions, i.e., waxed, at 20°C, and 100% relative humidity.

The changes in properties of all the samples stored under "standard" or "special" conditions were measured by periodic tests carried out over a 12 month period. At the end of the testing program on aging, one sample that had been left in the original Shelby tube for a period of 14 months was also tested.

## Results

### *Unwaxed samples*

After 3 months' storage in airtight plastic containers, in the presence of air, oxygen, and nitrogen, all samples were partially covered with white and orange mold and with brown to black spores. The clay, originally bluish gray in colour, had turned brownish. The samples had fissured and seemed stronger and stiffer as if they had dried, but measurement of the water content showed no significant change during the storage period. The undisturbed strength increased by 10–20% during aging. However, this might be due to the loss of sensitivity, which increases the adhesion along the fall-cone.

The remoulded strength increased markedly with time, whereas the liquidity index and the pH decreased, as shown in Fig. 5. The concentration of all ions in the pore water increased with time, with the exception of bicarbonate, which shows a downward trend beginning some 3 months after removal of the wax coating. The chloride concentration was found to remain very low during aging and for that reason has not been plotted. It is noteworthy that the use of nitrogen did not slow down the aging process. It appears that the amount of residual air in the container or possibly seeping through the "airtight" seal is quite sufficient to achieve considerable oxidation of the samples. In this regard, it should be pointed out that the greatest scattering in the results was obtained between two samples from about the same depth, stored 11½ months in the same $N_2$-filled plastic container.

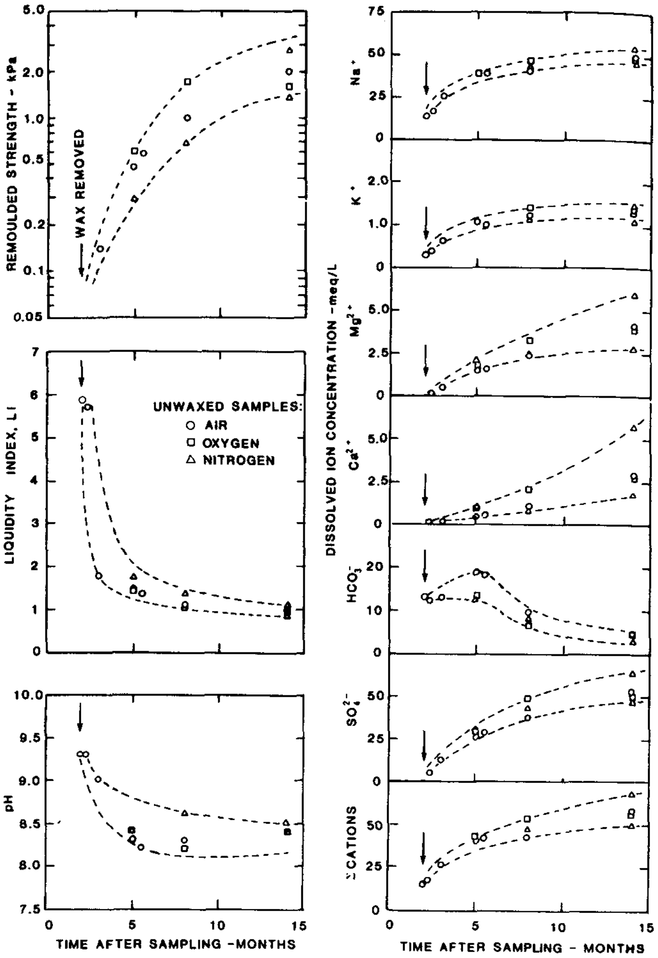


FIG. 5. Effect of time on the properties of samples unwaxed 2 months after sampling and stored in air, $O_2$, and $N_2$ at 20°C.

### *Waxed samples*

As shown in Fig. 6, the changes in geotechnical properties and pore water chemistry of waxed samples stored at 20°C were less pronounced than in unwaxed clay (Fig. 5). The wax slowed down the aging process but did not prevent it. With time, more

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[1] The gray (Gy) is the absorbed dose that is equal to one joule per kilogram (J/kg).

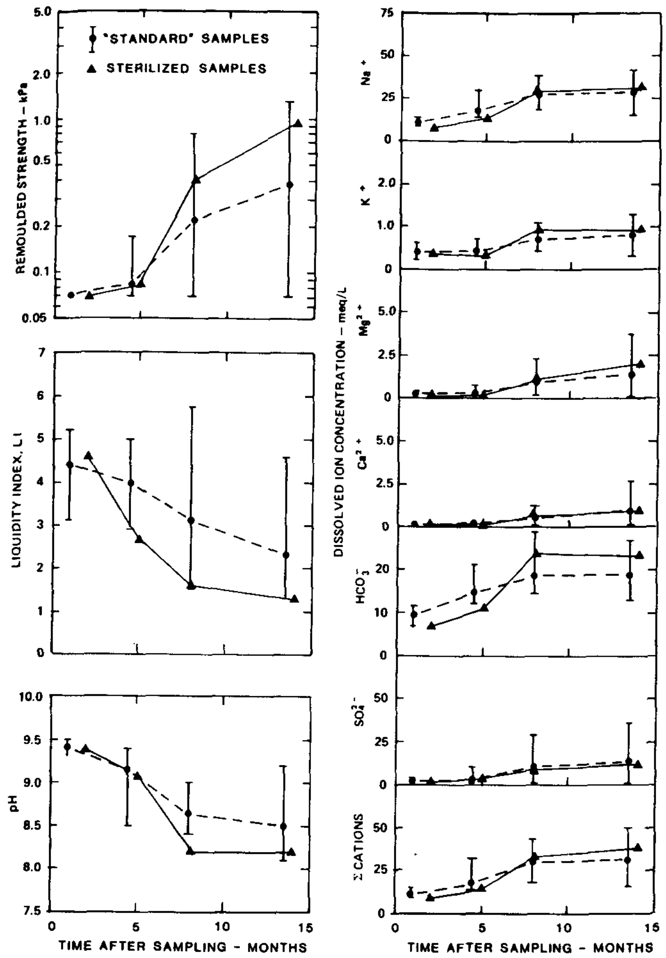

FIG. 6. Effect of time on the properties of waxed samples stored at 20°C. The brackets indicate the range of variation of the results and the circles represent the average value of each series of tests.

and more samples lost their quickness. This was always accompanied by changes in the colour and condition of the wax seal. Yellowish stains appeared in the originally white paraffin as diffuse spots randomly distributed over the sample or as lines, apparently along microfissures in the wax. These may originate from the attack of wax by organic acids formed as by-products of the oxidation of complex carbohydrates present in the clay. The formation of a black coating at the soil–wax interface was also observed, mostly at the ends of the samples where air is easily trapped between the wax and clay surface. This black X-ray amorphous compound is believed to be of organic origin. Under optical microscope it appeared to be formed of spores, which are known to grow in aerobic environments. In summary, the large scattering of the results shown in Fig. 6 seems to be due to the variable quality of the wax coating. Microfissures in the wax or air pockets trapped at the clay–wax interface resulted in a rapid oxidation of some samples, while some well-sealed samples showed little sign of aging even after storage for over a year.

In all the samples tested, the changes in the geotechnical and chemical properties of the material were accompanied not only by the presence of yellow or black stains in the wax but also by a change in the colour of the squeezed pore water. Initially colourless, it became gradually yellow as aging occurred. Since none of the measured ion concentration increases could account for the change in colour of the pore fluid, a determination of soluble iron and dissolved organic carbon (DOC) was made on 10 pore fluid samples showing various degrees of colour changes. In all the samples, the concentration of dissolved iron was below measurable value, which is in agreement with the low solubility of iron at the pH of the pore water (pH $\simeq$ 8.3). The dissolved organic carbon analysis of the pore water samples yielded values ranging between 17 and 95 ppm, higher values being measured in the yellowish fluids. No further analysis was carried out to identify the exact nature of the organic compound. However, there is a strong possibility that the yellow substance consists of fulvic or humic acid formed by the oxidation of organic matter as complex compounds are broken down into organic acids. It is likely that these organic acids are the source of the yellow stains appearing in the wax during aging.

### *Sterilized clay*

The values of the physicochemical properties of sterilized samples fall, with a few exceptions, in the range of variation obtained for the samples waxed and stored at 20°C as shown in Fig. 6. The samples tested 8 and 14 months after sampling exhibited higher alkalinity and lower pH, as compared with the average "standard" sample, apparently caused by oxidation of organic matter as indicated by the presence of yellow stains on the wax and the marked yellowish colour of the pore water. Although the dosage used was about five times that recommended for 100% sterilization, the irradiation of quick clay samples did not prevent aging from proceeding. It is therefore likely that aging is not directly mediated by bacteria. However, enzymes, which are smaller than bacteria and less sensitive to radiation (McLaren and Reshetko 1957), may act as catalysts in the oxidation process. Molds and spores are also more resistant to sterilization and might remain active after irradiation.

### *Effect of temperature*

The effect of temperature on aging of waxed and unwaxed samples is illustrated in Fig. 7. The physicochemical properties of the waxed samples stored at 4°C showed very little variation with time over a period of 1 year. No yellow stain was observed on the wax and the pore water remained colourless. The samples exposed to the air at 4°C showed clear signs of aging. They looked drier and stiffer but with no apparent loss of water content. Contrary to those stored at 20°C, however, no molds or spores were found on the samples. The pH also remained relatively high, and the bicarbonate showed no increase in the early stage of aging as observed at 20°C. This suggests that low temperature hinders the oxidation of organic matter. However, the increase of sulfate with time of exposure to air does not seem to be affected by storage temperature, as illustrated by Fig. 8. The figure also shows that in the first few months of aging the concentration of calcium is lower at 4°C, apparently because of the limited organic matter oxidation.

### *Sample kept in Shelby tube*

The last sample analyzed in the testing program on aging was the one shipped and stored in the Shelby tube. The sample had been prepared as follows: Immediately after sampling, 2–3 cm of clay was removed from the lower end of the tube and the tube was sealed by means of a plastic and rubber "Soilseal" covered with about 1 cm of wax. The other end was sealed by pouring 2–3 cm of wax in the tube. Upon reception, the sample was stored in a wet room at 20°C.

Fourteen months after sampling, the Shelby tube was opened and the clay tested. Surprisingly, the sample was found to be still extremely quick. The very high pH and low concentration

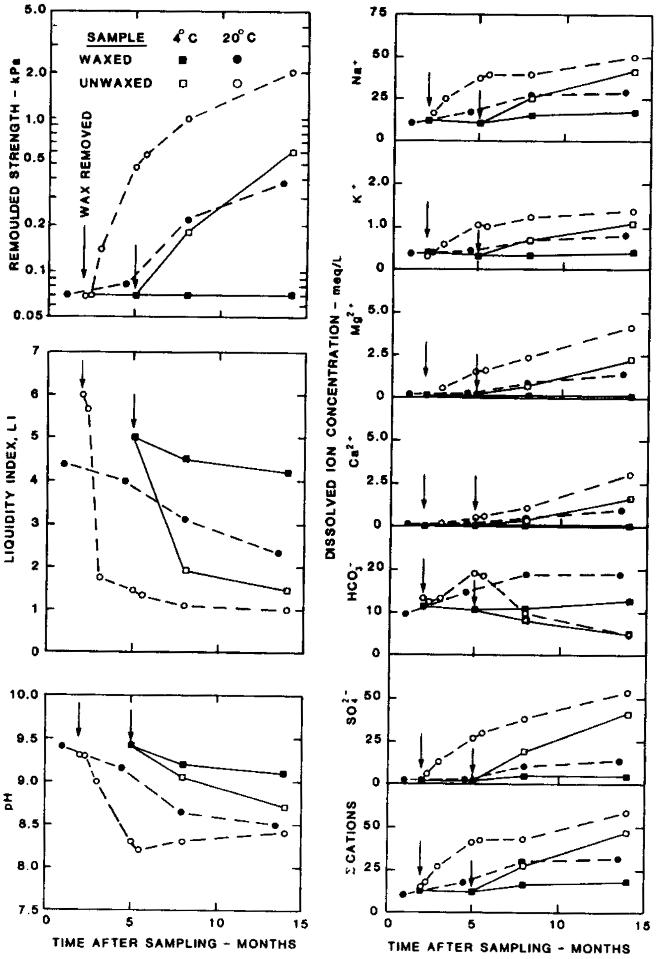

FIG. 7. Effect of time on the properties of waxed and unwaxed samples stored in air, at 4°C, and 20°C. The arrows indicate when the wax was removed from the samples.

of dissolved ions, particularly $SO_4^{2-}$, $Ca^{2+}$, and $Mg^{2+}$, indicated that virtually no aging had occurred in more than 1 year. A visual examination of the sample also showed no sign of alteration. The clay was medium gray, slightly bluish in colour; no brownish ring of oxidation was found on the periphery of the sample. The steel itself did not show any sign of oxidation inside the tube. Apparently, the thick wax caps are less susceptible to the formation of small fissures (possibly caused by handling or temperature change during transport and storage) than is the standard multilayer wax coating and thus provide a much better barrier against oxygen diffusion.

## Chemical processes in aging

The evolution of sulfate and bicarbonate concentrations with time in waxed and unwaxed samples suggests that two major oxidation processes take place in the clay during aging, namely the oxidation of organic matter and the oxidation of iron sulfide.

### *Organic matter oxidation*

As illustrated by Fig. 9, the bicarbonate concentration, for a given pH, is much higher in the waxed samples (solid symbols) than in the unwaxed samples (open symbols). This is due to the fact that the oxidation of carbohydrates or organic matter (generalized here as a simple formaldehyde $CH_2O$) produces $CO_2$ according to the general reaction

[1] $CH_2O + O_2 \rightarrow CO_2 + H_2O$

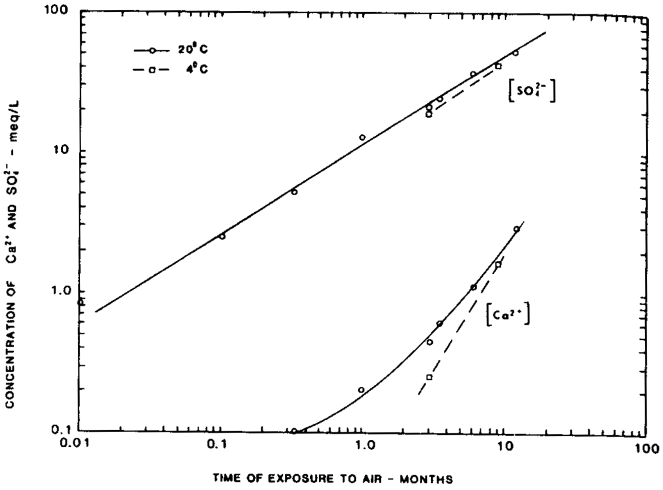

FIG. 8. Effect of time on the pore water concentrations of sulfate and calcium in samples exposed to air ($P_{O_2}$ = 20 kPa (0.2 atm)).

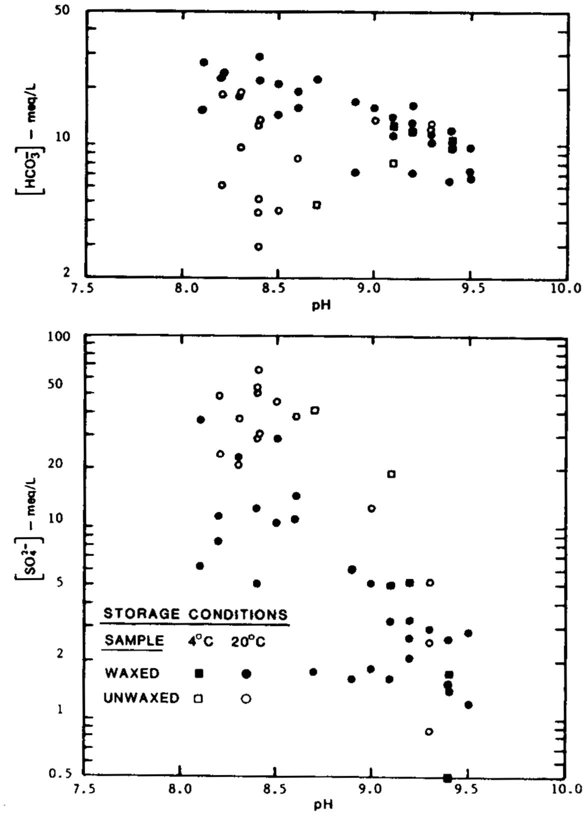

FIG. 9. Effect of soil pH upon the concentrations of bicarbonate and sulfate in the pore water of samples stored under various conditions.

In the waxed samples, $CO_2$ cannot escape and builds up. The increase in partial pressure of $CO_2$ results in the formation of a weak acid, $H_2CO_3$, which decreases the pH and increases the concentration of calcium and bicarbonate by dissolving calcium carbonate according to the reaction

[2] $H_2CO_3 + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^-$

The oxidation of organic mattter appears to be catalyzed by microorganisms such as spores or molds that show reduced activity at lower temperature. This is in agreement with the

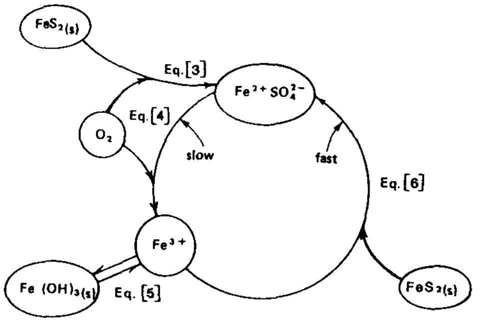

FIG. 10. Mechanism of pyrite oxidation.

absence of organic growth and the low bicarbonate production observed on the samples stored at 4°C.

*Iron sulfide oxidation*

In the unwaxed samples the $CO_2$ produced by the oxidation of carbohydrates is free to diffuse out of the sample and therefore has little influence on the pore water chemistry of the clay. The bicarbonate concentration remains low (Fig. 9). In these samples where oxygen is readily available, the drastic increase in sulfate concentration is believed to result from the oxidation of iron sulfide through a chain reaction as is illustrated by Fig. 10 which shows the various steps involved in the cyclical oxidation of pyrite. First, pyritic sulfur is directly oxidized by oxygen according to the equation

$$[3] \quad 4FeS_{2(s)} + 14O_2 + 4H_2O \rightarrow 4Fe^{2+} + 8H^+ + 8SO_4^{2-}$$

Ferrous iron is then oxidized to ferric iron by the reaction

$$[4] \quad 4Fe^{2+} + 4H^+ + O_2 \rightarrow 4Fe^{3+} + 2H_2O$$

The reaction in [4] occurs extremely slowly at low pH unless it is catalyzed by bacterial activity involving *Thiobacillus ferrooxidans* (Stumm and Morgan 1970; Zajic 1969). In the case of quick clays, the rate of reaction may be significant, even in the absence of bacterial activity because of the high pH of the material (Snoeyink and Jenkins 1980).

The ferric iron formed by the reaction in [4] may either precipitate as $Fe(OH)_3$ according to the reaction

$$[5] \quad 4Fe^{3+} + 12H_2O \rightarrow 4Fe(OH)_{3(s)} + 12H^+$$

or be available to oxidize more $FeS_2$ to $Fe^{2+}$ by the reaction

$$[6] \quad FeS_{2(s)} + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$

Once the pyrite oxidation has started, i.e. once a small amount of $FeS_2$ has been oxidized by $O_2$ ([3]), oxygen is involved only indirectly in the reoxidation of $Fe^{2+}$ to $Fe^{3+}$ ([4]). The oxidation of $FeS_{2(s)}$ ([3]) is no longer of significance, most of the $FeS_2$ being oxidized by $Fe^{3+}$ according to [6]. An ample supply of $Fe^{3+}$ for this reaction is guaranteed, because $Fe(OH)_{3(s)}$ precipitated by the reaction in [5] will be present right at the site of iron oxidation. The net result of pyrite oxidation is the formation of yellow $Fe(OH)_{3(s)}$, which causes the brownish discoloration of the samples. Based on a Eh–pH diagram representing the stability fields of iron in the presence of sulfur and carbonate, the level of oxygen for which $FeS_2$ becomes unstable relative to $Fe(OH)_3$ corresponds to a partial pressure of oxygen in the order of $10^{-65}$ kPa.

*Changes in pore water chemistry*

The global equation describing the oxidation of pyrite may be obtained by summing up [3]–[5], which yields

$$[7] \quad 4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 16H^+ + 8SO_4^{2-}$$

Similarly the oxidation of iron monosulfide follows the reaction

$$[8] \quad 4FeS + 9O_2 + 10H_2O \rightarrow 4Fe(OH)_{3(s)} + 8H^+ + 4SO_4^{2-}$$

In neutral or slightly acid waters, $Fe(OH)_3$ is essentially insoluble, and therefore the major changes in the pore water chemistry will be brought about by the formation of sulfuric acid, which causes a decrease in pH and alkalinity as the bicarbonate is neutralized by the strong acid according to the reaction

$$[9] \quad HCO_3^- + H^+ \rightarrow H_2CO_3$$

However, the system is buffered by the presence of calcite, which is gradually dissolved by the sulfuric acid following the equation

$$[10] \quad CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^-$$

The iron sulfide oxidation does not appear to be catalyzed by microorganisms, since neither sterilization nor low storage temperature had any effect on the rate of sulfate formation.

The scattering of the results observed in Fig. 9 is mostly due to the effect of the various storage procedures upon the oxidation of organic matter and iron sulfide. If the contribution of the two processes is taken into account by plotting the summation of $SO_4^{2-}$ and $HCO_3^-$ (which is approximately equal to the summation of cations given the low chloride concentrations) as a function of pH, a much better correlation is obtained (Fig. 11). Again, however, the higher concentrations are obtained in the unwaxed samples apparently because sulfuric acid predominantly produced in these samples is a strong acid and dissolves more $CaCO_3$ than does $H_2CO_3$. For similar reasons, the pore water concentration of calcium is also slightly higher in unwaxed samples at a given pH.

*Cation exchange*

Although the increase in the total salinity of the clay is due to the dissolution of $CaCO_3$ by carbonic and sulfuric acids, only a fraction of the cations found in the pore water is calcium, as shown by inference in Fig. 11. This is due to the cation exchange process which occurs in the clay. At the beginning of aging, i.e. at pH ≃ 9.5, the calcium makes up only 0.5% of the pore water cations. As aging goes on, most of the calcium produced by dissolution of calcite is adsorbed by the double layer. Gradually, an equilibrium is reached and more calcium remains in the "free" pore water. At a pH lower than 8.5, calcium makes up 5–10% of the dissolved cations.

Figure 12 shows how the dissolution of calcium and its increasing pore fluid concentration affects the concentration of sodium, potassium, and magnesium in the pore water. In the early stage of aging, the monovalent cations are preferentially displaced from the adsorbed system as predicted by the double-layer theory. The relationship between the calcium and magnesium concentrations is more linear because they have the same valence.

As shown in Fig. 13, the increase in salinity and particularly in the pore water concentration of divalent cations results in a decrease of the interparticle forces and leads to an increase in remoulded strength (Mitchell 1976).

*Effect of amorphous material*

Although the changes in geotechnical properties observed in the quick clay during aging can be adequately explained by the

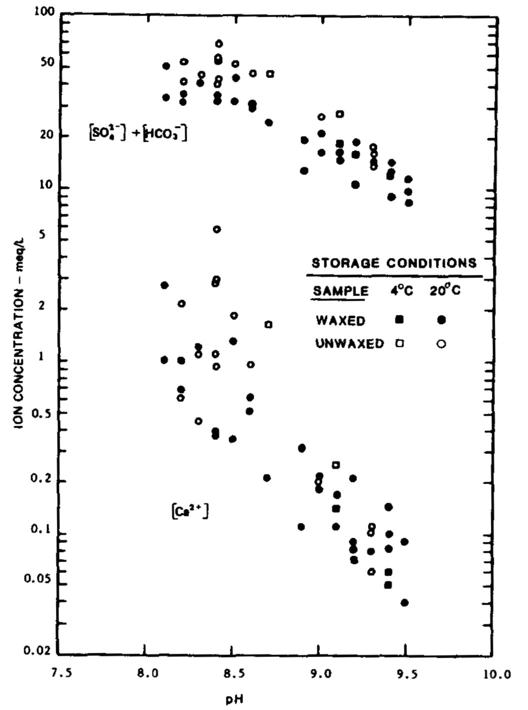

FIG. 11. Effect of soil pH upon the calcium and total ion concentrations in the pore water of samples stored under various conditions.

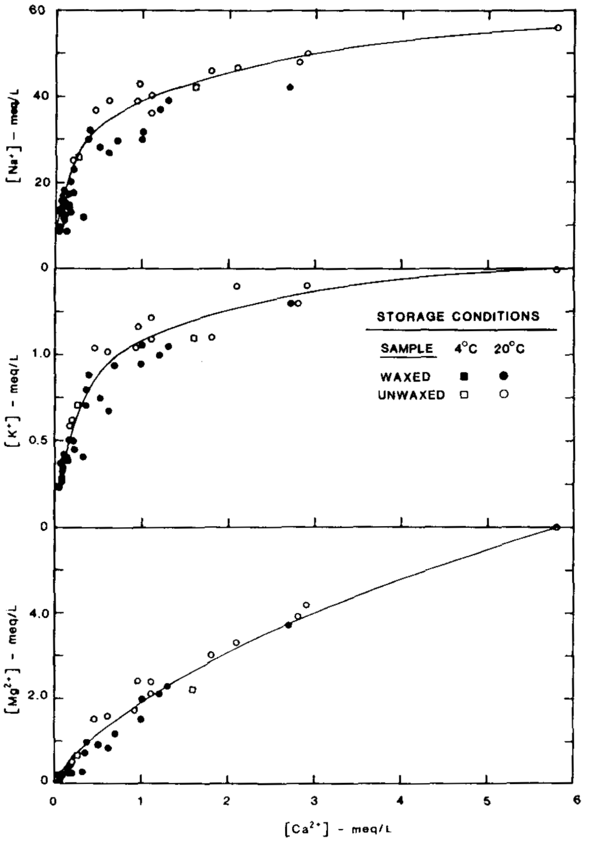

FIG. 12. Effect of dissolved calcium concentration upon the concentrations of sodium, potassium, and magnesium in the pore water of samples stored under various conditions.

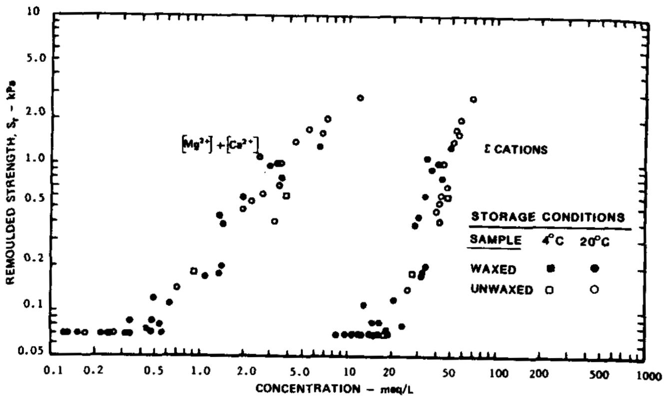

FIG. 13. Relationship between remoulded strength and the concentrations of divalent cations and divalent plus monovalent cations in samples stored under various conditions.

variation of the pore water chemistry, insoluble compounds may also contribute to the increase in remoulded strength. This is the case of iron hydroxide, $Fe(OH)_3$, formed during aging by the oxidation of iron sulfide. This compound, often referred to as amorphous material because of its poor crystallinity, is believed to increase the specific surface area of the clay, which results in a higher water-holding capacity (Loken 1970; McKyes *et al.* 1974; Yong *et al.* 1980). It also seems capable of regenerating the cementing bonds during shearing (Yong *et al.* 1979).

The amount of $Fe(OH)_3$ precipitated during aging may be estimated from the concentration of sulfate measured in the pore water, since for 1 mol pyrite oxidized, 2 mol sulfate and 1 mol iron oxide are produced. Also 1 mol iron monosulfide yields 1 mol sulfate and 1 mol hydroxide. This means that for a sample with a 50% water content and a sulfate concentration of 70 meq/L (the maximum concentration measured in 1 year of aging), 0.05–0.1% of Fe per dry weight of soil will be precipitated as $Fe(OH)_3$ by the oxidation of iron sulfide. Such an increase in Fe might lead to a slight increase in remoulded strength and liquid limit by increasing the specific surface area and the cation exchange capacity (Hendershot and Carson 1978). The contribution of $Fe(OH)_3$ to remoulded strength is likely to increase as aging proceeds.

It is very difficult to estimate the amount of $Fe(OH)_3$ present in the clay other than by calculation. The selective dissolving technique (Yong *et al.* 1979) often used to estimate the amount of amorphous material is not believed to be adequate to detect such a small increase in $Fe(OH)_3$ in the clay. In effect, the method, which is based on alternate washing of the clay with 0.5 $N$ NaOH and 8 $N$ HCl, results in an overestimation of the amount of $Fe(OH)_3$ actually present in the soil, as the strong acid causes the oxidation of FeS and possibly of a large part of $FeS_2$. Crystalline $Fe_2O_3$ and $Fe_3O_4$ present in relatively low quantities may also contribute to an overestimation of the amorphous compounds. Whether these crystalline oxides may act as cementing compounds is not known. As pointed out by Quigley (1980), the selective dissolution technique also results in the dissolution of chlorite and illite, which is likely to cause an overestimation of amorphous alumina and silica unless appropriate corrections are made. These facts should be kept in mind when examining the relationship between sensitivity and the so-called amorphous compounds.

## Conclusion and recommendations

The physicochemical properties of a clay from La Baie were found to be typical of Champlain quick clays: very low plasticity, liquidity index greater than 3, sensitivity greater than 50, and pH of about 9.5. The mineralogy is characterized by the abundance of primary or "rock flour" minerals such as feldspar, quartz, amphibole, and calcite, and by illite as the principal clay mineral. The dissolved pore water chemistry consists predominantly of sodium bicarbonate. Low concentrations of sulfate, calcium, and magnesium and high alkalinity and pH are attributed, in part, to the anaerobic sulfate-reduction process taking place *in situ*. This process is believed to be controlled by the bacterially catalyzed decomposition of organic matter and results in the formation of metastable iron sulfide.

Some signs of aging were observed in all the quick clay samples stored in the laboratory, regardless of the method of storage. With time, the remoulded strength and liquid limit increased and the sensitivity, liquidity index, and pH decreased. The water content, plastic limit, and undisturbed strength remained practically unchanged. The pore water concentrations of calcium, magnesium, and sulfate increased severalfold.

From the test results it is postulated that the aging of quick clays occurs as follows: In the presence of oxygen, the organic matter is oxidized to form carbonic acid, which dissolves calcium carbonate, thus increasing the concentration of calcium and bicarbonate in the pore water. In the meantime, pyrite and (or) iron monosulfide are oxidized to sulfuric acid and yellow iron hydroxide, which imparts a brownish colour to the oxidized clay. The sulfuric acid produced by the cyclical oxidation of iron sulfide neutralizes the bicarbonate and dissolves $CaCO_3$. A large proportion of the dissolved calcium is adsorbed in the double layer, thereby displacing sodium, potassium, and magnesium from the adsorbed system to the free pore water. The increase in salinity and especially in divalent cations resulting from the dissolution of $CaCO_3$ reduces the interparticle repulsive forces and increases the remoulded strength.

None of the storage procedures studied was found to be entirely satisfactory. Any sample stored in the laboratory will eventually undergo significant changes in pore water chemistry and in geotechnical properties. Consequently, it is recommended that the clay be tested as soon as possible after it is obtained from the field.

If it is necessary to store quick clay samples for a period in excess of a few months, certain measures may be taken in order to minimize the rate of aging. The following storage procedures are suggested:

(1) The samples should be stored at 4°C to reduce the organic matter oxidation to a minimum and prevent rapid deterioration of the wax coating.

(2) Quick clay samples in Shelby tubes may be stored in the tube if the steel is in good condition (no rust). The tube should be sealed with thick wax caps (2–3 cm) at both ends to reduce the oxygen diffusion.

(3) Samples extruded from the Shelby tube should be waxed with many layers of wax. Special care should be taken not to trap air pockets between the clay and the wax.

(4) Block samples should be precut to the size needed for the test to be carried out in the laboratory, and then waxed individually, in order to avoid exposing the entire block to air every time a test is to be performed.

It is recommended to measure the pH of the clay at the time of sampling or at the reception of the samples, in order to monitor the aging of clays stored in the laboratory. In effect, the pH is very sensitive to oxidation in the early stages of aging. Furthermore, its measurement was found to be simple and reproducible if the same method is used for all tests.

For determining the pore water chemistry of marine clays, not only should the extraction of the pore water be done soon after sampling but the chemical analysis should also be carried out as soon as possible after squeezing the water out of the sample, in order to minimize potential contamination by the aging of solid particles in suspension in the squeezed pore water. If storage becomes necessary, the water extract can be frozen to slow down the rate of oxidation of organic matter and iron sulfide.

## Acknowledgments

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