

SWELLING OF CLAY UNDER PRESSURE

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ABSTRACT

An experimental technique for studying the swelling of clay under constraint and some preliminary results for the swelling of Wyoming bentonite in several media are presented and discussed. Fractionated, powdered clay is mixed with an equal weight of non-swelling microporous porcelain, which serves to distribute the swelling agent rapidly and uniformly. The mix is compacted in a cell at high pressure and permitted to imbibe fluid through a porous porcelain plate under simultaneously applied almost equal pressures from 0 to 10,000 psig on both sides of the fluid-gel interface. The unidirectionally constrained volume change of the sample is measured by displacement of mercury in a steel buret. Degree of swelling is taken as the volume ratio of gel to 105° C dry clay.

In the range of pressure from 0 to 10,000 psig, the colloidal magnesium sodium montmorillonite swells from about 93 to 231 percent (volume ratio 1.93 to 3.31) depending on the composition of imbibed fluid. Aqueous 0.171N sodium chloride and magnesium chloride solutions produce 14 and 11 percent, respectively, more swelling at 1,500 than at 0 psig. Swelling in calcium chloride solution is insensitive to this pressure change. At 10,000 psig these solutions, and hydrochloric acid, produce less swelling than at 1,500 psig and, in fact, produce almost equal swellings of 130 ± 4 percent. It is inferred that swelling in chloride solutions at this pressure may be essentially cation-independent. Within the concentration range of 0 to 1.71N there appears to be little practical difference in the degree of swelling of the clay by sodium chloride and calcium chloride solutions; the swelling is a linear function of the logarithm of the salt concentration.

Comparison of $d(001)$ spacings calculated from swelling ratios with those obtained by X-ray diffraction lead to the conclusion that the method measures crystalline swelling in contradistinction to osmotic swelling.

INTRODUCTION

The production branch of the petroleum industry is interested in the swelling properties of clays because these minerals occur widely in oil producing rocks (Nahin, Merrill, Grenall and Crog, 1951). With their relatively large surface areas the clays are capable of affecting significantly the flow of oil to producing wells. In primary production it is important to maintain the greatest oil permeability in the maximum drainage volume immediately surrounding the borehole; in secondary recovery, the aim is to obtain optimum injectivity of flood water through the injection wells. In both operations the degree of hydration of the clays in the vicinity of the borehole affects the efficiency of the process. It is important therefore to know how, and to what extent, the various fluids introduced into wells during their drilling, maintenance, or use as secondary injectors affect the physical volume of the clays.

As is well known, there is considerable literature devoted to the clay-water relation and swelling (Brindley, 1951; Cardwell, 1954; Foster, 1953; Grim, 1953; Hermans, 1949; Hendricks, Nelson and Alexander, 1940; Katz, 1933; Kister, 1947; Marshall, 1949; Mering, 1946; Overbeek, 1952; *Trans. Faraday Soc.*, 1946). However, nearly all of this work concerns systems at atmospheric pressure and under conditions far removed from those thought to exist in a petroleum reservoir. The closest published approach to the type of swelling study described in this paper was that by Power, Towle and Plaza (1942). They measured the pressure developed by a confined plug of Wyoming bentonite as a function of the amount of fluid, at atmospheric pressure, imbibed through a paper blotter. This is the classical swelling experiment of Posnjak (1912) in which the gel volume is held constant. In the present study of clay swelling as related to oil reservoirs it appeared necessary to recognize that in the reservoir both clay and fluids exist in a high pressure isobaric environment. Furthermore, because the volume of a gel is less than the volume sum of the separate phases (Katz, 1933) and, secondly, because pressure favors diminution of volume, according to the law of van't Hoff and Le Chatelier, simultaneous pressure on both liquid and gel should increase swelling. The swelling system described herein was designed to realize this process.

The main purpose of this paper is to report the development of an apparatus for studying clay swelling at constant pressure in the range of pressure from atmospheric to 10,000 psig. The results obtained on a Wyoming bentonite with this instrument are considered as preliminary in nature and form only part of a reconnaissance study of clay swelling under a variety of conditions, some of which may be encountered in reservoir operations.

MATERIALS, APPARATUS AND PROCEDURE

The "Wyoming" bentonite from Belle Fourche, South Dakota, used in all of the tests as a "typical montmorillonite" was obtained from the Baroid Division of National Lead Company. A less-than 0.2-micron fraction was prepared from a 2 percent suspension of the clay in distilled water by centrifugation in a Sharples supercentrifuge. Analysis of this fraction indicated a magnesium-sodium-calcium ion exchange clay with 39, 38 and 17 milliequivalents per 100 gm., respectively. This exchange composition might be expected to typify the clay surface in an oil reservoir containing a medium-hard connate water. Total cation exchange capacity of the clay by the ammonium acetate method is 94 meq./100 gm.

The samples used in the swelling tests consist of a mixture of 4.50 gm. each of 105° C dried powdered clay and smaller-than 50 mesh ball-milled Selas 06 microporous porcelain. The latter, of maximum pore radius 0.30-micron, serves as fluid distribution medium and is obtained by crushing 3-inch diameter $\times \frac{3}{8}$ -inch thick discs supplied by Boder Scientific Company, Pittsburgh, Pennsylvania. The weighed, thoroughly mixed sample is compacted in the swelling cell (Fig. 2) at 1,820 psi by means of a calibrated

heavy duty spring compressed by a manually operated hydraulic jack. The filled-cell is then depth-gauged for calculation of sample volume. The porosity is determined by helium displacement following which the cell is connected to the swelling unit (Fig. 1). A thin surgical rubber or neoprene diaphragm separates the mercury-clay interface. The sample is evacuated to 0.001 mm. mercury pressure and, as is indicated in Figure 1, nitrogen is introduced to pressure the system to 1,500 psig, the swelling agent is admitted to the sample through the porous Selas 06 disc (Part D, Fig. 2), and the height of the mercury column in the calibrated stainless steel buret is recorded at the beginning of the run and usually daily thereafter until an apparent equilibrium is reached. In operation at 10,000 psig the method is similar except the storage cylinder of a pressure intensifier is charged with about 11,500 psi of nitrogen which, over a period of less than a minute, is leaked to the swelling unit previously pressured to 1,500 psig from a standard nitrogen bottle.

Upon admission of the swelling fluid the clay begins to swell, apparently immediately. Progress of the swelling is manifested by the displacement of a $\frac{1}{8}$ -inch diameter soft iron ball lying atop the column of mercury in the buret. The position of the ball is located by a magnetic induction coil sliding on the steel buret. The $\frac{1}{8}$ -inch thick $1\frac{1}{2}$ -inch diameter coil of No. 34 magnet wire wound on a lucite spool forms one arm of an 11,000 cycles per second impedance bridge. Balance is shown by null indication on a Hewlett-Packard Model 400C vacuum tube voltmeter. The ball can be located to within ± 1 mm.; calibration values for the eight burets used varied in the range 20-23 cm./cc.; displacements ranged from about 2-70 cm.

CALCULATION OF SWELLING

The quantitative expression of swelling is defined here as the Swelling Ratio, SR, given by the equilibrium volume ratio of gel to dry clay. Symbolically,

$$SR = \frac{V_g}{V_c} = \frac{V_c + p + \Delta V_o}{V_c} = 1 + \frac{\rho_c}{M_c} (p + \Delta V_o),$$

where

V_g = volume of clay gel at end of run

V_c = volume of clay solid phase at 105° C

p = porosity, or void volume of clay-Selas mixture, available to clay gel

ΔV_o = volume change of clay-Selas mixture upon swelling as observed on buret

ρ_c = solid phase density of clay by helium displacement

M_c = weight of 105° C dried clay in sample.

The porosity available to clay gel is obtained from the relation,

$$p = V_b - V_c - V_d - V_1 = V_b - V_{He} - V_1 = V_b - V_{He} - 0.268_5 M_d,$$

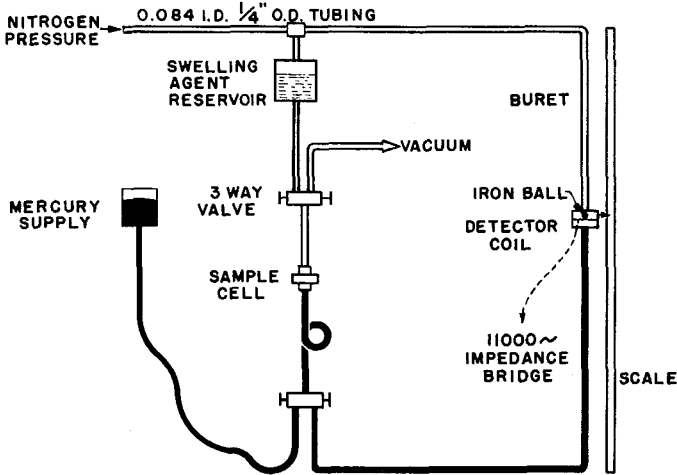


FIGURE 1. — Schematic diagram of high pressure clay swelling unit.

where

- V_b = bulk volume of clay-Selas mixture
- V_d = volume of Selas solid phase
- V_i = volume of internal pores of Selas not available to clay gel
- V_{He} = helium displacement of dry sample before swelling (sum of solid phase volumes of clay and Selas)
- M_d = weight crushed Selas.

The factor, $0.268_s M_d$, is V_i and was determined in a separate helium-mercury displacement experiment on crushed Selas 06. From measurement of the mercury displacement at a series of pressures in the range 500 to 1,300 mm. the internal porosity of the Selas not available to clay gel at 760 mm. was computed to be 0.268_s cc./gm. This amounts to the tacit assumption that the space not available to mercury at one atmosphere pressure is the same as that unavailable to clay gel.

Experimentally, the helium displacement V_d , of the crushed Selas was found to be 0.367 cc./gm. Hence, the density of the clay is

$$\rho_c = \frac{M_c}{V_c} = \frac{M_c}{V_{He} - V_d} = \frac{M_c}{V_{He} - 0.367 M_d}$$

From the foregoing, it is evident that the percent swelling may be expressed as

$$\% Sw = \left(\frac{V_g}{V_c} - 1 \right) 100 = (SR - 1) 100.$$

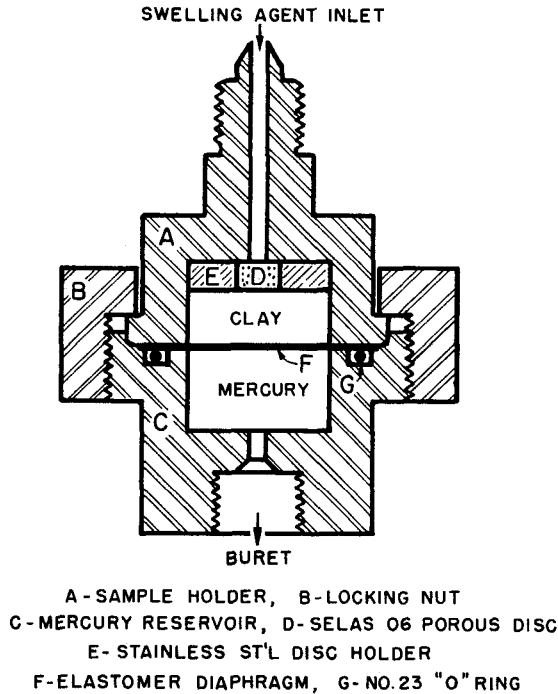


FIGURE 2. — High pressure swelling cell.

In using these formulas it is assumed that the Selas microporous porcelain, fused during manufacture at temperatures up to 2,650° F, does not swell. Experimental evidence that the presence of Selas does not sensibly affect the evaluation of the effective porosity of the sample is adduced from the results of porosity determinations on Wyoming bentonite compacted with and without an equal part of Selas 06. With Selas absent the density was calculated to be 2.625 gm./cc. In determinations on five different samples with 1:1 clay-Selas the densities were 2.64, 2.68, 2.56, 2.67, 2.65; average 2.64 gm./cc.

RESULTS AND DISCUSSION

The data on swelling of fractionated Wyoming bentonite in various media are summarized in Table I.

In the range of pressure from 0 to 10,000 psig, the colloidal magnesium-sodium montmorillonite swells from 93 to 231 percent (volume ratio 1.93 to 3.31) depending on the swelling agent composition. In no case was the minimum observable swelling of 32 percent ($\Delta V_o=0$, $p=0.55$ cc., $\rho_c=$

TABLE I. — SWELLING OF WYOMING BENTONITE AT 25° C

| Swelling agent | Swelling agent concentration | Pressure, psig | SR.10 ^a |
|---|------------------------------|----------------|--|
| HOH | 100% | 1,500 | 331±5 ¹ (3) ^a ↑* |
| HOH | 100% | 10,000 | 272±1(2) |
| (NaPO ₃) ₆ | 0.171N | 1,500 | 326±7(3) ↑ |
| C ₁₂ H ₂₂ O ₁₁ | 10% aqua | 1,500 | 316±7(8) ↑ |
| NaOH | 0.171N | 1,500 | 309±12(3) ↑ |
| NH ₄ OH | 15N | 1,500 | 199±1(3) |
| CH ₃ OH | 100% | 1,500 | 201±6(4) |
| HOCH ₂ CH ₂ OH | 100% | 1,500 | 193±3(3) ↑ |
| HCl | 0.171N | 1,500 | 265±5(3) |
| HCl | 0.171N | 10,000 | 228±4(4) ↑ |
| CaCl ₂ | 0.171N | 0 | 256±6(4) |
| CaCl ₂ | 0.171N | 1,500 | 255±5(4) |
| CaCl ₂ | 0.171N | 10,000 | 236±4(4) |
| CaCl ₂ | 0.171N | 1,500 | 291±5(4) |
| CaCl ₂ | 1.71N | 1,500 | 226±7(3) |
| NaCl | 0.171N | 0 | 237±10(4) |
| NaCl | 0.171N | 1,500 | 251±9(7) |
| NaCl | 0.171N | 10,000 | 224±3(5) |
| NaCl | 0.0171N | 1,500 | 310±12(4) |
| NaCl | 1.71N | 1,500 | 214±7(4) |
| MgCl ₂ | 0.171N | 0 | 231±6(4) |
| MgCl ₂ | 0.171N | 1,500 | 242±2(4) |
| MgCl ₂ | 0.171N | 10,000 | 231±3(3) |
| LiCl | 0.171N | 1,500 | 241±4(4) |
| NH ₄ Cl | 0.171N | 1,500 | 232±2(4) |

¹ Arithmetic average deviation from the average SR.

² Number of samples tested.

* Arrow up denotes equilibrium not reached, SR still increasing at end of run.

2.64 gm./cc., $M_c = 4.50$ gm.) noted. Thus, this clay swells measurably in all swelling agents tested, *viz.*, all values of SR exceed 1.32.

In all experiments the initial rate of swelling was very great. It was not unusual for from 70 to 90 percent of the swelling to occur within a relatively few minutes after joining the two phases. The remainder of the swelling to an apparent equilibrium took from three to six days for the chloride solutions to over seven weeks for deionized water. (Constant buret reading for two days was taken as indicative of swelling equilibrium). Apparently, the rate of swelling depends mainly on the rate of accessibility of clay surface.

Mechanism

The slowing down of the rate of swelling may be consistent with a two-step mechanism: first, the majority of the platelets are in direct surface contact with at least one micropore of the porcelain thus ensuring almost instant contact between fluid and the surface ions or lattice charges be-

lied to be responsible for swelling; and secondly, the minority of platelets having contact only with other platelets are hydrated by the relatively slow process of diffusion of fluid through the surrounding gel formed in the first step. These relations, which may exist between the clay and the microporous porcelain before and after swelling, are shown in the idealized sketch, Figure 3.

Effect of Pressure

The effect of hydrostatic pressure on swelling of Wyoming bentonite in 0.171N solutions of hydrochloric acid and three common salts is shown in Figure 4. Concentration of 0.171N was chosen because this corresponds approximately to the ionic strength of a 10,000 ppm sodium chloride brine, characteristic of certain California reservoir waters. However, it must be noted that with the recorded average fluid imbibition of 3 to 4 cc., this

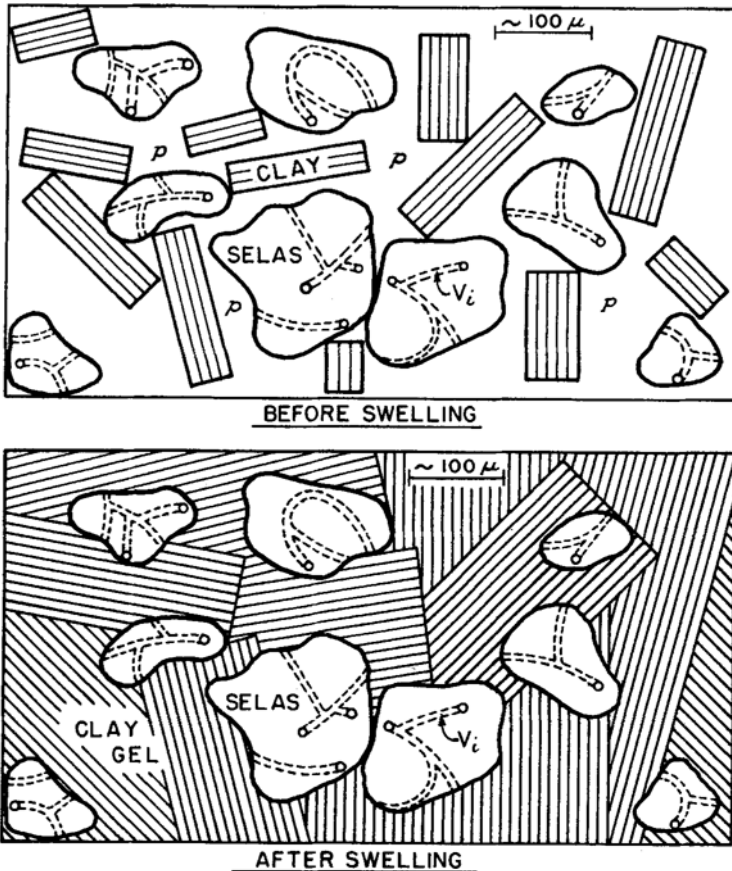


FIGURE 3.—Porosity relation in clay-microporous porcelain system (idealized).

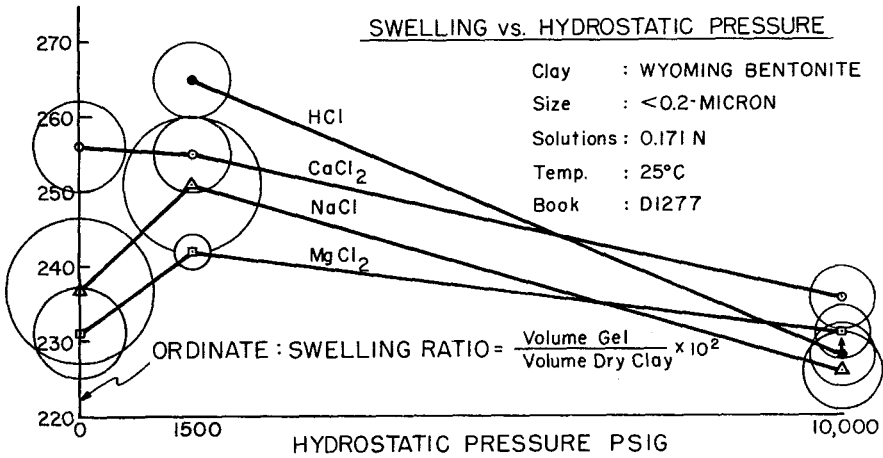


FIGURE 4. — Swelling vs. hydrostatic pressure.

amounts to 0.5 to 0.7 milliequivalents of solution ions in contact with 4.23 milliequivalents of surface exchange ion, assuming 100 percent permeation. This is an average solution: clay ionic concentration ratio of only about 14 percent and must be given proper weight in considering the effects suggested by the observed swelling ratios. The upper limit of 10,000 psig pressure was chosen for two reasons: ease of laboratory management and, more importantly, it encompasses pressure conditions currently found in petroleum production. Also, it substantially exceeds the maximum swelling pressure of 4,500 psig recorded by Power, Towle and Plaza. The straight lines of Figure 4 are purely speculative and are not meant to imply that the swelling ratio is a maximum at 1,500 psig. Possibly the maximum occurs above 1,500 psig in view of the observation of Power, Towle and Plaza (1942) that, typically, their unfractionated Wyoming bentonite ceased absorbing liquid at approximately 1,800 psig. Nonetheless, Figure 4 indicates somewhat greater swelling at 1,500 psig than at 0 psig or 10,000 psig. Swelling in calcium chloride solution appears relatively insensitive to pressure change. It is interesting that at 10,000 psig all of these solutions produce almost equal swellings of 130 ± 4 percent; perhaps swelling in chloride solution at this pressure is essentially cation-independent. If so, this would tend to confirm the expectation of Norrish (1954) from X-ray studies that after montmorillonite has completed the first (9.6 Å to below 22 Å) and second stages of crystalline swelling to a (001) spacing greater than 35 Å (which, from the data of Norrish and Quirk (1954) would be predicted in 0.171N salt solutions), the swelling is essentially osmotic and independent of cation for ions of the same valence. Indeed, from Figure 4, even the valence may not be of considerable importance.

On the other hand, if one takes 9.6 Å as the basal spacing of unhydrated

montmorillonite and neglects swelling at the platelet edges, a swelling ratio of 2.30 (130 percent swelling) amounts to a c-axis expansion to only 22 Å. (For a 1,000 Å long by 200 Å wide dry platelet the edge area is less than 5 percent of the basal area.) The maximum observed swelling ratio (non-equilibrium, to be sure) of 3.31 would indicate a c-axis expansion to about 32 Å; the minimum observable swelling ratio of 1.32, an expansion to 12.7 Å. On this basis perhaps not all of the crystalline swelling mentioned by Norrish was completed under the conditions of these experiments.

It is important to note here the enormous volumetric differences between free "swelling" in an open system, with the attendant maximum opportunity for osmotic dilution of the gel micelles to over a thousand percent in some cases, and the constrained swellings of the present experiments to a maximum of less than 250 percent. Comparison of $d(001)$ spacings calculated from swelling ratios with those obtained by X-ray diffraction (Table II) lead to the conclusion that the method measures crystalline swelling in contradistinction to osmotic swelling.

The effect of pressure on swelling in water (Table I) may be appreciable and indicates, perhaps, that the swelling pressure is less than 10,000 psig. If, in fact, equilibrium was reached at 10,000 psig it might be inferred that swelling pressures could be readily determined with this apparatus from the maxima of plots of swelling ratios versus applied hydrostatic pressures.

Effect of Concentration

The effect of varying concentration upon swelling at 1,500 psig was studied with sodium and calcium chloride solutions (Fig. 5). Within the range of 0 to 1.71N there appears to be little difference in the degree of swelling in these solutions. This finding seems to conflict with the assertion that exchange of monovalent ions against divalent ions decreases swelling (Overbeek, 1952). Perhaps, the present result is a reflection merely of the

TABLE II. — COMPARISON OF C-AXIS EXPANSIONS OF WYOMING BENTONITE FROM SWELLING RATIOS AND X-RAY DIFFRACTION

| Fluid | SR at 1,500 psig | $d(001)$ by SR, Å | $d(001)$ by XRD, Å |
|--------------------------------------|---------------------------|-------------------|------------------------------------|
| HOH | 3.31 \uparrow^1 | >32 | <22-crystalline } >35-osmotic } |
| HCl 0.171N | 2.65 2.28 \uparrow^3 | 25.4 21.9 | 22.5 (<0.5N) ² |
| CaCl ₂ 1.71N | 2.25 | 21.6 | 18.7 (2N) ² |
| NaCl 1.71N | 2.14 | 20.5 | 18.7 (1N) ² |
| CH ₂ OH | 2.01 | 19.3 | 17.3 (EtOH) ⁴ |
| HOCH ₂ CH ₂ OH | 1.93 \uparrow | 18.5 | 17.0 ⁴ |

¹ Arrow up denotes equilibrium not reached.

² Norrish, 1954.

³ Data for 10,000 psig.

⁴ Bradley, 1945.

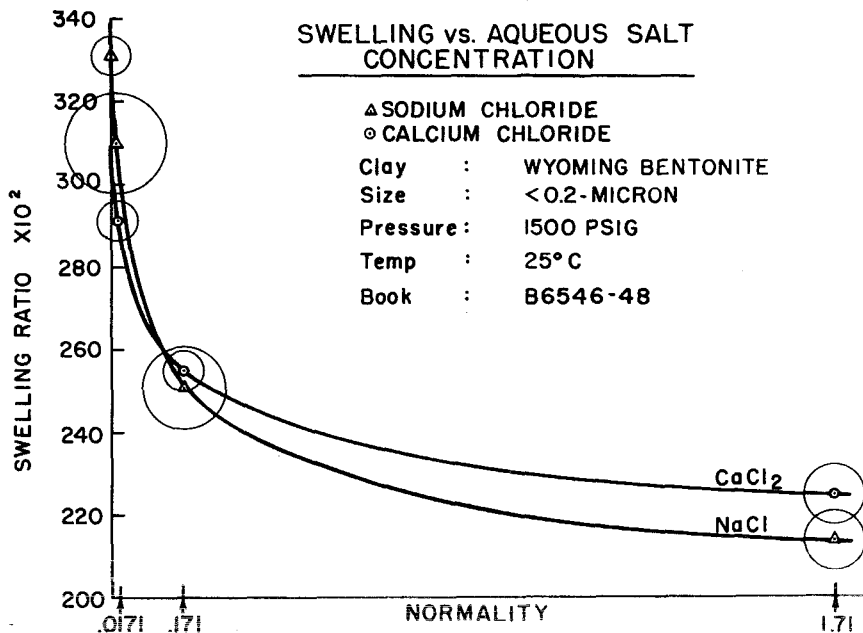


FIGURE 5. — Swelling vs aqueous salt concentration.

large amounts of both calcium and sodium ions in the clay surface relative to the solution. Plotted semi-logarithmically, the data for NaCl from 1,000 to 100,000 ppm fit the straight-line equation:

$$SR = 4.54 - 0.481 \log_{10}(\text{NaCl}),$$

where (NaCl) is concentration in parts per million of NaCl. This equation indicates that should the relation hold down to, say, about 1 ppm, the swelling ratio in essentially pure water, might be in the neighborhood of 4-4.5; experimentally, the observed non-equilibrium value was 3.31.

Effect of Hydroxyl

The results for sodium hydroxide, ammonium hydroxide, and sodium hexametaphosphate indicate that alkalinity may be a pro-swelling factor. The ten percent sucrose solution was run to determine whether such a hydroxylated but uncharged molecule in high concentration might lower the activity of the water sufficiently to depress the degree of swelling; the observed swelling ratio appears to be about the same as for deionized water. Absolute methyl alcohol and anhydrous ethylene glycol gave swelling ratios of 2.01 and 1.93, respectively. These amount to estimated c-axis expansions to 19.3 Å and 18.5 Å which approximate, roughly, the 17 Å spacings for ethylene glycol and ethanol observed with X-rays (Bradley, 1945).

Limitations of the Method and Results

Emphasizing again the preliminary nature of these results it is clear that the method has certain limitations and that, within these limitations, some improvements are possible. The limitations on measurement of degrees of swelling below about 32 percent is a severe one. Improvement in this regard for tests at 25° C does not appear promising; experiments with Selas 06: clay ratios of less than unity resulted in undesirable increases in time required to reach swelling equilibrium. This defeats the purpose of the micro-porous porcelain of facilitating rapid, uniform saturation of the clay by fluid. Raising the test temperature to 100° C and higher will increase the rate of swelling and thereby enable lowering the amount of Selas required for completion of runs within specified time intervals. Thus, at the higher temperatures it should be possible to determine the smaller degrees of swelling. The variation of the swelling with temperature will, of course, depend on whether the process is exothermic or endothermic. Variations in the degree of inhomogeneity of the Selas-clay mixture is believed responsible for the different average deviations recorded. Better means for mixing the two solids should reduce this source of error and, thereby, permit greater precision in determination of swelling ratio with fewer runs per sample.

It is likely that some of the relatively small spread of the exploratory data presented here may be a consequence of the unfavorable ionic concentration ratio of clay : solution; greater differences among the various solutions may become evident at ratios of unity and higher. In the present experiments, because of exchange, the original-cation concentration in the liquid phase at equilibrium was certainly below 0.171N in that cation. More readily interpretable results would be obtained by the swelling of surface-homionized clays in solutions of like cation and at a clay : solution ion symmetry of near unity.

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