

thicknesses for which this approximation will hold will be structure dependent, dependent on the microscope acceleration voltage and will become more accurate for higher voltages, although at higher voltages for the same contrast more defect of focus will be required.

The type of approximation in scattering theory to be used is also going to vary with the structure being examined. Although in this structure, and for comparatively thin crystals, large two-dimensional multislice calculations were used to obtain a good fit with experiment, this may not always be necessary. In fact, although the smaller two-dimensional multislice calculation and the systematic multislice calculation from a two-dimensional phase grating were quite poor with regard to calculation of diffracted beam intensity as a function of crystal thickness due to heavy weak-beam absorption, images calculated from both these methods are in reasonable agreement with experiment after the effects of the various aberrations are included. In similar structures even simpler methods may apply. In particular, calculations made on $\text{TiNb}_{24}\text{O}_{62}$ show that the systematics multislice from a one-dimensional phase grating is adequate.

The effect of instrument aberrations can be included in calculations in a systematic fashion and the principal effect is, as one might expect, that of averaging and blurring out of detail in the images.

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The Effect of Freezing on Precipitating Solids

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The major effect of a freeze/thaw treatment on aqueous gels, sludges or slurries is a decrease in crystallite size either by compressive or shear stresses, built up as a consequence of the increase in volume during the water to ice phase transformation. This change in crystallite size together with the freezing potential developed, leads to a reduction or neutralization in the positive particle charges, which results in accelerated precipitation on thawing.

Introduction

Settling, sedimentation or filtration of precipitating solids, particularly if gelatinous, is a tedious, time-consuming laboratory chore and in industry can be a major problem, particularly in the case of water treatment. Here the disposal of the by-product, (a sludge containing variable quantities of miscellaneous solids

and water, according to the district and type of water treatment employed), can account for more than half the total treatment cost (Swanwick & Davidson, 1961). In addition valuable land must be used for settling lagoons, to limit bulk handling of drained material.

Any change in the handling of precipitating solids, therefore, leading to substantial savings in time or cost, would be of enormous benefit. Such a change was

introduced by Regan, Stephenson & Clements (1948) when they patented a sludge treatment process involving a freeze/thaw step in the filtration cycle, which led, after much shorter handling times, to a considerable decrease in the water content of the final sludge.

Briefly, they found that if high water-content, slowly settling sludges were frozen and thawed before filtration, then flocculation, sedimentation or precipitation rates were increased, often by more than two orders of magnitude. This, with the standard ferric sulphate or aluminum sulphate flocculation additives (Sims & Carmen, 1971), gave a further, more efficient sludge treatment cycle.

It is not clear what takes place during the freezing process described and a brief review of the literature only highlights various aspects of the problem but, as will be seen, provides no solution.

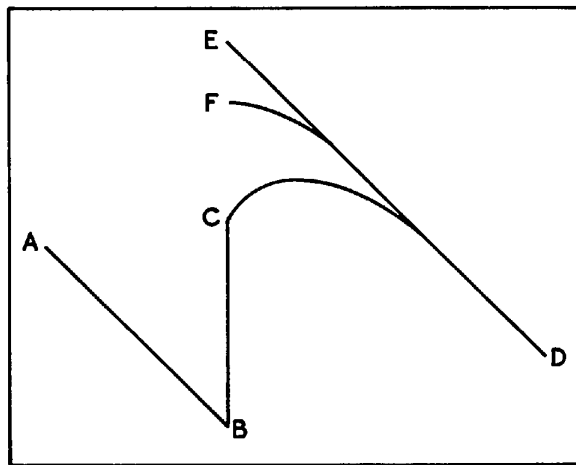


Fig. 1. Diagrammatic. ice volume increase.

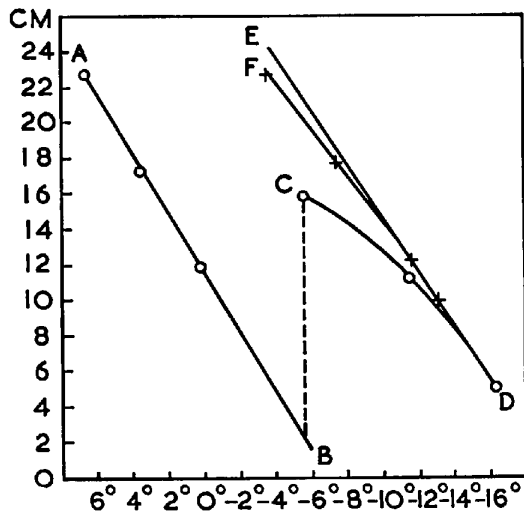


Fig. 2. Alumina and water (54.46% water). (After Foote & Saxton, 1915.)

For example, Villiers (1895) observed that the gelatinous blue-green flocs of basic copper hydroxide, $\text{CuO} \cdot \text{OH}$, formed by the addition of sodium carbonate to copper sulphate solution, settled as a turquoise blue crystalline precipitate on melting, after having been frozen for two hours. He also noted that the process became more effective the longer the gel remained under the supernatant liquid before freezing and suggested that the granulation effect after thawing might be due to pressure of ice formation; or as Villiers put it

'Peut-être ces transformations doivent-elles être attribuées à la compression exercée par la dilatation de la glace qui emprisonne les précipités; . . . , où il a dû certainement subir une pression considérable.'

Later, Bruni (1905, 1915) reported the dehydration of silica gels by freezing, while Foote & Saxton (1915), gave quantitative data on the dehydration of aluminum hydroxide gels by successive freezing and thawing. They also reported that the gelatinous precipitates became granular after freezing and that little effect was noted above a temperature of -6°C .

The method used by Foote & Saxton to follow the freezing process is of great interest, being an early example of the use of 'cryogenic' volume dilatometry. The dilatometer, half filled with the mixture under test, was filled to the mark with ligroin, a high vapour pressure mixture of paraffin hydrocarbons. The expansion of this fluid recorded the volume expansion of ice formed on freezing.

Thus, the line AB in the diagram in Fig. 1 shows the normal contraction before freezing, BC the sudden expansion when freezing begins, CD the expansion and contraction on further cooling and DE the expansion and contraction as the temperature is raised, DE being the linear extension of the heating curve from D . Since the lines AB and DE proved to be nearly parallel experimentally, they chose the length of the vertical at -6° as a measure of the expansion and by the use of Bunsen's (1870) data, that 1 g of water at 0° expands 0.09070 cm^3 on freezing, they calculated the total weight of frozen water. They also suggested that gels contained 'free', 'capillary' and combined water which of course could not freeze and that the line BC corresponded to the amount of free and some capillary water and CE represented the major quantity of capillary water present; sharp differentiation between the 'two varieties of water' being impossible due to super-cooling effects!

Fig. 2, an experimental curve of the expansion of a drained aluminum hydroxide gel on freezing, shows the method in use.

By this technique they were able to determine variations in water content of gels prepared by different routes, they noted an effect due to aging and also recorded progressive dehydration by successive freeze/thaw cycles, without reabsorption of water on standing which they found took place in the case of silica gel.

It must be pointed out that the effect they reported as being due to aging of the aluminum hydroxide gel also occurs if the gel is allowed to stand under the supernatant fluid at room temperature. Mellor (1946) reports extensively on the structural changes from an amorphous to a crystalline state of these gels under these conditions, and goes so far as to state that the formula $\text{Al}(\text{OH})_3$ is rarely if ever reached stoichiometrically, the OH content varying with preparation, pH, and time *etc.*

The next citation of interest is an amusing warning by Ewe (1920) to other members of the American pharmaceutical profession, on the disastrous effects of too cold a shop in winter. In his words then:

'When magnesia (mixture) magma is frozen and thawed again, the stable milk-like appearance is altered and a clear, colorless liquid, with a thick sediment results. This is due to the conversion of the normal water content of the magnesium hydroxide gel into ice crystals with the result that the gel condition is disturbed and the molecules of magnesium hydroxide unite to form a fine crystalloid powder. This form is practically irreversible. . . .'

and he goes on to quote other medicaments placed at risk in a cold shop.

Hepburn (1926) examined the rate of dehydration with time of freezing, using aluminum, ferric and cupric hydroxide gels, and Fig. 3 shows that appreciable dehydration took place with increase in freezing time. The effect of gel condition was also studied and is shown in Fig. 4. Here curve *A* is for frozen ferric hydroxide in the presence of supernatant fluid, curve *B* represents the freezing of drained gel and curve *C* is for a frozen, freshly precipitated, centrifuged gel, suspended in distilled water. It is apparent that within the limits of experimental error curves *B* and *C* are identical. The product of the freeze/thaw treatment, in both cases, was extremely coarse.

Syōhei (1940) of Japan confirmed that granular precipitates were formed after freezing hydrogels of Al, Fe, Ni, Zn and Cu and suggested that this structural change might be due to a state of strain in the particles, set up by the ice pressure. Later he also noted (Syōhei, 1941) that filtering time for aluminum hydroxide gels was considerably reduced as a result of freezing.

Hazel (1946) in a study of the effect of freezing on the stability of silica sols found that maximum separation by flocculation took place in 15 min except between the acidic pH range 2.5-3.5, as seen in Fig. 5. This is unlike the behaviour of aluminum hydroxide, which progressively dehydrates with freezing time. He also found that coagulation time was a function of pH (see Fig. 6). These results may explain the reabsorption of water by silica gels noted by Foote & Saxton (1916), who also reported an aging effect.

As an example of one of many papers on the dehydration of clays, Kayser & Bloch (1947) reported that the thixotropic characteristic properties of suspen-

sions of Bentonite clays in water were destroyed by freezing and if this were sufficiently prolonged it led to flocculation after thawing. The bentonite clay is a mixture of montmorillonite, $\text{Al}_4\text{Si}_8\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$, and beidellite, $\text{Al}_2\text{Si}_8\text{O}_{20}(\text{OH})_4$, the unknown quantity of water, $n \cdot \text{H}_2\text{O}$, being loosely bound, some say between clay layers. An effect due to freezing would not be a surprise under these conditions.

As has already been stated, Regan *et al.* (1948) patented their freeze/thaw sludge treatment process and in 1950 they published an article on applications of their work (Regan, Stephenson & Clements, 1950), reporting that additions of the standard flocculants, ferric sulphate and aluminum sulphate, improved freeze/thaw filtration speeds. Finally in 1955 they patented the improved process in the U.S.A. (Regan, Stephenson & Clements, 1955).

Following this work, Isaacs (1965), in a review article on the principles of waste water treatment, re-

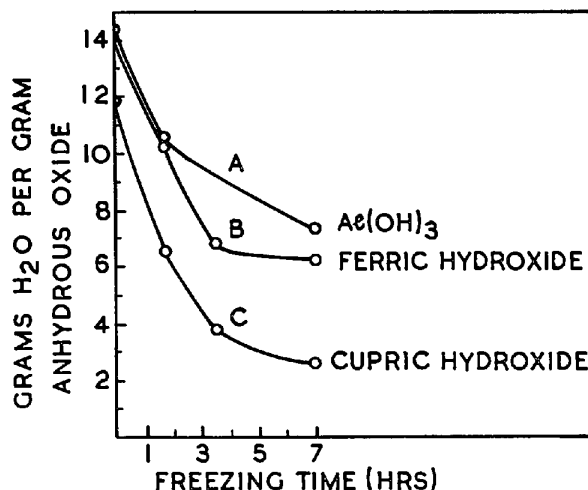


Fig. 3. Rate of dehydration with time of freezing.

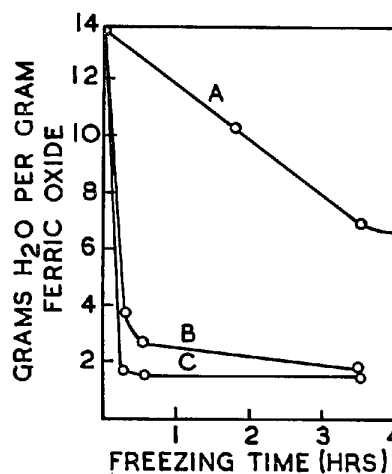


Fig. 4. Dehydration of types of washed and drained gel. (After Hepburn, 1926.)

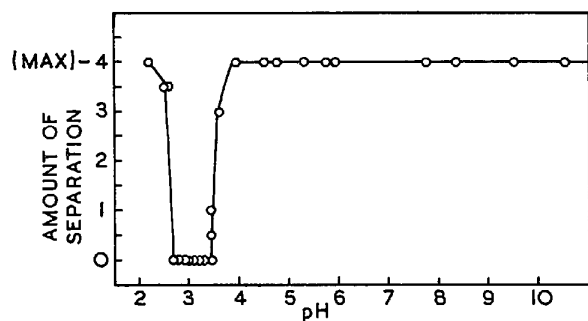


Fig. 5. Flocculation after 15 min freezing at various pH values.

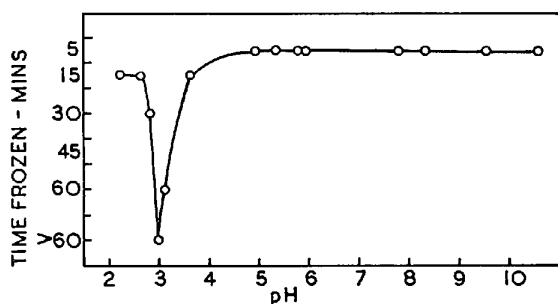


Fig. 6. Coagulation time by freezing at various pH values. (After Hazel, 1926.)

ported that the freeze/thaw treatment reduced the specific resistance to filtration by a factor of 10^3 . This parameter, specific resistance to filtration, is described in a paper by Swanwick & Davidson (1961) and is a rather loose way of measuring the filtration characteristics of suspensions, slurries and sludges; for a fuller description see the Appendix.

Finally, to bring the subject up to date we have a review article on the dehydration of sludges by Gale (1971) and a paper by Logsdon (1971) on the mechanism of the dehydration of water-works sludges by freezing, in which he suggests that solids are pushed out of the water as the ice front advances. He also states that there is little or no relationship between particle rejection and ζ potential or particle size. He may well be right about particle rejection at the ice front. A similar explanation has been put forward by Barnes (1928) to explain salt rejection on freezing seawater where the brine is found not in the ice but between ice crystal boundaries. Impurities in metals are also invariably found along grain boundaries.

The only other reference involving a practical use of freezing treatment in any industrial process other than the numerous uses developed in the food industry was found in the preparation of theoretically dense polycrystalline alumina prepared from cryochemically processed powders. Here, Kim & Monforte (1971) describes the freezing of a water suspension of aluminum hydroxide, followed by sublimation of the ice, *in vacuo*, producing an intimately dispersed and uniform material ready for subsequent furnace treatment.

Thus, from this review of the literature on freezing precipitating solids, four important aspects emerge: that a freeze/thaw process changes gels or sludges *etc.* to granular particles, that this results in a marked increase in rate of precipitation, that dehydration is a measurable effect and that an ageing process may play a significant part in the mechanism.

Obviously, what happens to the precipitating particle is of prime importance and it is the object of this work to extend our knowledge in this direction.

Samples of representative gelatinous precipitates will be compared with typical water-works sludges and examined by X-ray diffraction powder analysis, both before and after freezing, in an attempt to identify structural change, if any, crystallite size being examined by 'line broadening' techniques. The work will be monitored by reference to geological specimens of similar chemical constitution.

2. Standard materials . Experimental detail

Samples of magnesium hydroxide and aluminum hydroxide were examined using the techniques of Debye-Scherrer X-ray crystallography and powder analysis, as fully discussed in a paper by Flint (1966). To relieve the eyestrain which invariably accompanies the analysis of large numbers of X-ray powder pattern negatives, a powder scanner developed by the author in 1968 was used.

These hydroxide samples were prepared from 10% w/w solutions of magnesium sulphate, aluminum chloride, and aluminum sulphate in distilled water, just neutralized by the addition of ammonium hydroxide solution. The neutralized solutions, containing the coagulated hydroxides were divided into two equal portions, one of which was filtered, washed and the precipitate dried in an air oven at 50°C , and the other portion frozen at -18°C for 24 hours. The frozen portion, in a polythene bottle to yield to the expansion of ice, was then thawed, filtered, washed and dried in a similar manner.

In parallel with this work powder specimens of brucite, $\text{Mg}(\text{OH})_2$, bauxite, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ and gibbsite, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, were prepared from good quality geological specimens, for the purposes of subsequent comparison.

All prepared specimens were then placed in turn in the X-ray diffraction camera, exposed for 8, 12 and 16 hr, when necessary, with a cobalt target, to photograph their characteristic X-ray powder patterns. A cobalt target was chosen because preliminary experiments showed that water-works sludges were often contaminated with sufficient iron oxide *etc.* to cause serious fogging of films prepared with the customary copper target. Standard powder patterns of substantially iron-free geological specimens, *etc.* were photographed for the purposes of rapid comparison and the cobalt target was used throughout.

In order to measure crystallite size from an X-ray

powder pattern it is necessary to know the width of any given line and of course any change in width if 'line broadening' has arisen due to any structural change. To do this one must have a knowledge of the optical density of the line, from edge to edge, which can be obtained with an X-ray densitometer. An X-ray densitometer can be very expensive, of the order of £1500 plus, and so a small experimental densitometer was made.

A 6 V, 30 W light source was focused onto the powder pattern film to give a spot of light 1 mm diameter, at the film centre. The film, held in a rigid jig on a rack and pinion, was then traversed horizontally along its length, such that 2 cm per min travel matched 2 in of chart speed on a Honeywell recorder connected to the output of a barrier layer Evans electroselenium cell, with a 1 mm Perspex cone tip to focus the light beam coming through the film. The film traverse was arranged to give approximately 10 in (25.4 cms) of travel, to cover the relevant detail.

It is of course appreciated that the instrument described can only be used for relative measurement and that film exposure conditions must be kept constant, since a variation here, such as too great an exposure, would lead to a low signal level across the low impedance required to retain linear response. Linear accuracy of film traverse was found to be ± 0.1 mm.

Thus the line width of strong lines in each powder pattern was measured in the manner described and from this data crystallite size and any changes due to the freeze/thaw treatment were calculated.

3. Standard materials. Results

(a) X-ray powder patterns of $Mg(OH)_2$

Fig. 7 shows positive reproduction of the X-ray diffraction powder patterns of natural brucite, freshly precipitated magnesium hydroxide and the same material after freeze/thaw treatment. The line *P* in the natural brucite pattern is either due to an impurity showing the strong line of $d=2.92$ or $d=3.09$, corresponding to $I_1/I_0=100$, for the monoclinic substances,

hydrated magnesium carbonate or coesite, SiO_2 , respectively, the resolution being too poor to identify from the single line.

The lines *A* and *B* in the patterns of hexagonal $Mg(OH)_2$ before and after freezing correspond to $d=4.8$, at *hkl* spacing 001, and $d=2.36$, at *hkl* spacing 101, respectively, and it is obvious that these lines are considerably broadened after the freeze/thaw treatment, indicating some degree of structural change. Powder pattern data for the magnesium hydroxide pattern shown in Fig. 7 are given in Table 1. Here line spacing data from the *A.S.T.M. Index* (1960) are compared with experimental measurements of '*d*' spacings, together with appropriate Bragg angles.

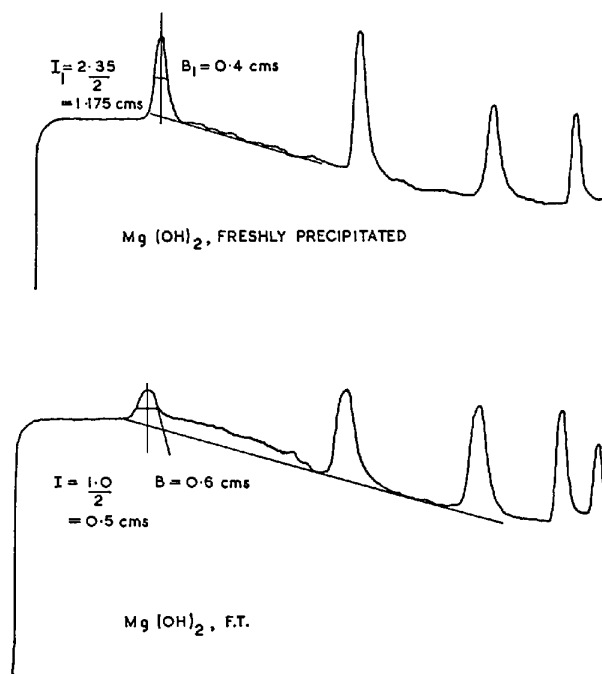


Fig. 8. Photometric traces of X-ray powder pattern of $Mg(OH)_2$, before and after freezing.

Table 1. Powder pattern data for brucite, $Mg(OH)_2$ structure: hexagonal

Values from <i>A.S.T.M. Index</i>			Bragg angle θ				
Spacing of lattice planes d_{hkl} (Å)	I_1/I_0 %	<i>hkl</i>	Experimental Values of <i>d</i> (Å)	Error %	(mm)	(°)	(radians)
4.77	90	001	4.80	+0.6	21.8	10.9	0.19024
2.725	6	100	2.70	-0.8	38.8	19.4	0.33859
2.365	100	101	2.36	-0.4	44.5	22.25	0.38833
1.794	56	102	1.78	-0.6	60.0	30.0	0.52360
1.573	36	110	1.57	0	69.8	34.9	0.60912
1.494	18	111	1.499	+0.7	73.9	36.95	0.64490
1.373	16	103	1.38	+0.7	81.5	40.75	0.71122
1.363	2	200	-	-	-	-	-
1.310	11	201	1.32	+0.8	86.5	43.25	0.75485
1.192	2	004	1.18	-0.8	98.2	49.10	0.85696

(b) *Crystallite size*

Now Bunn (1961) in his book *Chemical Crystallography*, defines the breadth of an X-ray powder line, in an 'ideal' powder photograph of a narrow specimen with a very narrow beam, as the angular width between the points at which the intensity falls to half its maximum value and he gives the relationship between this 'breadth at half height' β and the size of the crystals:

$$\beta(\text{in radians}) = \frac{C\lambda}{t} \sec \theta \quad (1)$$

where t is the thickness of the crystal, C is a constant, λ the X-ray wavelength, and θ the Bragg angle. Further work on crystallite size may be seen in the reports of Scherrer (1917), Seljakow (1925) and Bragg (1933), who give values for the constant C of 0.94, 0.92 and 0.89 respectively. Since these values are all of the order unity, Jones (1938) has suggested that the quantity ' t ' should be obtained from the formula

$$L_c = t = \frac{\lambda}{\beta \cos \theta} \quad (2)$$

and should be called the 'apparent' crystal size.

Since all crystals smaller than about 10^{-5} cm diameter give a broadened diffracted beam it is necessary to know the breadth of lines given by crystals greater than 10^{-5} cm, under the same camera conditions, in order to make a reference correction. It is the custom to mix annealed molybdenum powder with specimen under test to provide a standard line breadth of crystals greater than 10^{-5} cm, (see Jones & Peggs, 1971), but since in this work only relative measurements are made of crystallite size changes, the line widths of specimens were compared with standards from powder patterns of geological specimens of similar composition.

For the reasons given above, Henry, Lipson & Wooster (1951), point out that no great accuracy can be claimed for the method of assessment of the breadth of any line which is not likely to be more accurate than 5%, but for the purposes of comparison it may be used with confidence.

Fig. 8 shows the photometric traces of the powder patterns of freshly precipitated magnesium hydroxide and of the same material after freeze/thaw treatment

Table 2. *Crystallite size of three forms of brucite, Mg(OH)₂*

State	Line Width (mm)	L_c Observed (Å)	L_c Corrected (Å)	Reduction factor
Geological Brucite	0.79	260.2		
Freshly precipitated	1.57	132.9	260.2	} 2.0
'Freeze thawed'	2.36	88.0	132.9	

respectively. From these the breadth of the line at Bragg angle $10^\circ 54'$ or $d=4.77$ has been estimated and the respective crystallite sizes L_c have been calculated, as shown in Table 2. Corrected values, against natural brucite, were 260.2 Å for freshly precipitated Mg(OH)₂ and 132.9 Å after freezing, which is equivalent to a reduction in crystallite size by a factor of 2.

(c) *X-ray powder pattern of Al(OH)₃*

From their X-ray powder diffraction patterns it was clear that crystallite size in the aluminum hydroxide gels examined varied with pH, source, age and temperature of freezing and drying.

Fig. 9 shows a powder pattern of a hydroxide gel precipitated from Al₂(SO₄)₃ by neutralization, to the end point, with ammonium hydroxide. Zone A corresponds to the strong lines of an aluminum oxysulphate present as an absorbed impurity, which is quoted in the *A.S.T.M. index*, roughly as Al₄SO₄(OH)₁₀.5H₂O. Zones B, C, D and E correspond to 'broadened' d ' spacings of 3.2, 2.2, 4.7 and 1.5 Å respectively. This particular gel dried as a pearly-white translucent solid with a conchoidal fracture and was labelled 'crystalline' for identification.

A comparison of Figs. 9 and 10 shows that a definite structure develops in an aluminum hydroxide gel on standing, after a week in this case (as quoted in Mellor, 1946) and from Fig. 11 it is apparent that this change in structure is associated with the formation of hydrated natural oxides, since a significant number of lines in the powder patterns of bauxite, Al₂O₃.2H₂O, and gibbsite, Al₂O₃.3H₂O, can be seen in the powder pattern of aged aluminum hydroxide.

Finally, in Fig. 12, we see a comparison of a fresh precipitate of aluminum hydroxide, frozen at -18°C and one frozen in liquid air at approximately -190°C . It appears, at first glance, that the 'line broadening' effect is not so marked after liquid-air freezing.

All the results are collated in Table 3 and in each case a significant decrease in L_c , the crystallite size, is recorded. No hard and fast values can be taken from this table since it must be remembered that the resolution of the powder lines is very poor in the case of gel structures, as indeed can be seen in the powder patterns shown, but the values of L_c quoted can be taken as an estimate of crystallite dimensions. It is of interest to note here that freezing in liquid air did not lead to the smallest crystallite size and this agrees with industrial experience where no advantage has been found with freezing temperatures lower than -20°C .

At this stage the effect of freezing on water of crystallization was considered and Fig. 13 shows a comparison of the X-ray diffraction powder pattern of Na₂CO₃.10H₂O, before and after freezing. Apart from the spotty effect always seen with highly polycrystalline substances, of large crystallite size, there appears to be a distinct 'line broadening'. However, as sodium carbonate is very hygroscopic and also effloresces, depending on a high or low humidity in the ambient

atmosphere, it was considered that the ground powder in the 0.5 mm X-ray capillary tube may well have recrystallized, giving a smaller crystallite size. Further work in this direction would be of interest.

Viscous sludges. Experimental detail

(a) Sludge characteristics

Two extreme varieties of sludge were examined, one a typical fast-filtering calcite water-works sludge of specific resistance to filtration some $20 \times 10^6 \text{ sec}^2 \cdot \text{g}^{-1}$ labelled 'X' sludge and a viscous sludge labelled 'Y' with a specific resistance of $2000 \times 10^6 \text{ sec}^2 \cdot \text{g}^{-1}$, (for further comment see the Appendix).

To determine whether the particles in the two sludges X and Y carried an electrical charge they were filtered through a 3.5 cm sintered glass disc of porosity 11×1 covered with a platinum gauze electrode, as shown in the diagram in Fig. 14 and potential/volume-filtered data collected.

Finally, the water content of the viscous sludge Y was determined gravimetrically, both before and after freezing, to determine extent of dehydration, if any.

(b) Structure and crystallite size

Samples of sludge were filtered, dried in air at 50°C in a hot air oven, and ground. X-ray diffraction powder patterns were photographed in the manner described. From these, crystallite sizes were calculated.

5. Viscous sludges. Results

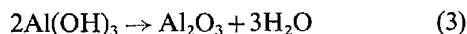
(a) Sludge characteristics

The electrofiltration experiments showed no change in filtration rate, for either X or Y sludge, with the platinum gauze electrode as anode, but gave the results shown in Fig. 15 when acting as cathode.

It is clear that a cathodic gauze increased the filtration rate with increase in potential for both types of sludge, and therefore sludge particles must carry a positive charge, but further than this one cannot go from these preliminary results, as sludge precipitation and filtration is a function of many kinetic forces.

The gravimetric analysis of sludge dried in air at 50°C before and after freeze/thaw treatment, gave losses of 37.0 and 48.9% volatiles respectively on ignition at 500°C for 4 hr. Thus the freezing treatment led to a further loss of volatiles of 11.8%.

Assuming that the reaction, on ignition, were



then a one molecule loss of water would be equivalent to 11.5% loss in weight of the gel.

Thus, within the limits of experimental error, the 11.8% extra loss of volatiles recorded, after a freeze/thaw treatment, could be equivalent to the mixing of an extra molecule of loosely retained water with the gel by some pressure mechanism during freezing.

This extra water would be retained in the capillaries

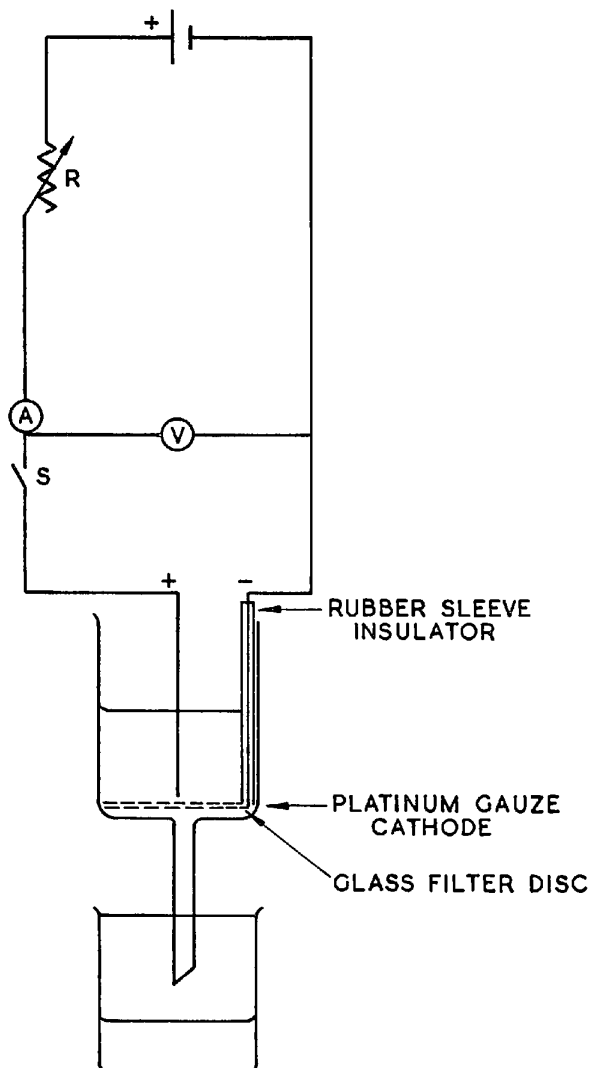


Fig. 14. Diagram of electrofiltration apparatus.

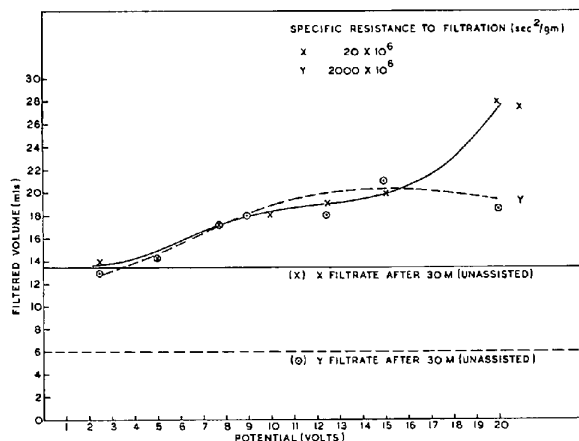


Fig. 15. Electrofiltration of gelatinous precipitates.

Table 3. *Crystallite size of various forms of Al(OH)₃*
From powder lines at observed Bragg angle of 15°45'.

State	Object of examination	Line width (mm)	L_c observed (Å)	Reduction factor
Geological Gibbsite Al ₂ O ₃ ·3H ₂ O	Line width correction	0.98	268.7	-
Al(OH) ₃ ex AlCl ₃ Dried at 50°C	Normal precipitation	0.70	265.3	1.71
As above 'Freeze-thawed' Dried at 50°C	Effect of freezing	1.38	154.8	
Al(OH) ₃ ex AlCl ₃ Dried at 115°C	Effect of dehydration temperature	1.10	193.4	1.25
As above 'Freeze-thawed' Dried at 115°C	As above	1.38	154.8	
Crystalline Al(OH) ₃	Effect of controlled precipitation	1.57	135.5	4.30
As above 'Freeze-thawed'	As above	6.69	31.7	
Al(OH) ₃ Frozen in liquid air	Effect of freezing temperature	2.6	97.7	2.71
Al(OH) ₃ ex AlCl ₃ One week under supernatant	Effect of time on structure	0.79	265.3	2.96
As above 'Freeze-thawed'	As above	2.36	89.7	

or interstices of the gel or precipitate on melting, being infiltrable, because of surface tension effects, but capable of easy evolution on ignition. A similar 'extra water effect' was reported by Foote & Saxton (1915), in their work on 'free', 'capillary' and combined waters in aluminum hydroxide gels observed during freezing, by their 'cryogenic' volume dilatometry technique.

It must be remembered that the viscous gel *Y* is not a pure aluminum hydroxide gel but a mixture of other things, as can be seen in Table 4, (a full analysis of *Y* water-works sludge), thus a deviation from the behaviour of pure aluminum hydroxide gels on freezing, where dehydration was noted, need not confuse.

Table 4. *Analysis of viscous sludge Y*

(After T. Finneccy, AERE, 1971.)
Specific resistance to filtration $2000 \times 10^6 \text{ sec}^2.\text{g}^{-1}$.

Material	% w/w
CO ₂	10.2
Loss on ignition (2 hrs. at 800°C)	45.4
SiO ₂	3.5
Fe ₂ O ₃	4.9
CaO	6.4
Al ₂ O ₃	38.9
Mg	Trace

(b) *Structure and crystallite size*

The water-works *X* sludge, with a low specific resistance to filtration of $20 \times 10^6 \text{ sec}^2.\text{g}^{-1}$, was floccu-

lated by the addition of copperas, a mixture of ferric sulphate and chloride, and some lime additive.

The powder patterns in Fig. 16 shows that the sludge, both before and after freezing, has an identical structure to that of calcite. Some slight line broadening is apparent after freezing and little change in crystallite size was recorded. It is of interest that sludges of this type benefit least from a freeze/thaw treatment, being readily filterable without.

The water-works *Y* sludge, with a high specific resistance to filtration of $2000 \times 10^6 \text{ sec}^2.\text{g}^{-1}$, was flocculated by the addition of aluminum sulphate and produced a sludge with a much less determinate structure. Fig. 17 shows a comparison of the powder patterns of sand and calcite with the *Y* sludge, after drying in air at 50°C and exposing to the X-ray beam for 8 hours. Clearly sand and calcite constitute definite sludge components, confirmation being given in Table 4 where 3.5% SiO₂, 6.4% CaO and 10.2% CO₂ are given as constituents.

Fig. 18 is a comparison of the powder patterns of *Y* sludge, before and after freezing, with an aluminum hydroxide gel, after similar treatment. An X-ray exposure of 12 hr resolved the Al(OH)₃ gel component of this sludge. Similar resolution of this component can be obtained by drying the *Y* sludge in air at 110°C, as can be seen in Fig. 19.

Table 5 gives estimates of the crystallite size of various forms of *Y* sludge, at observed Bragg angle 28°75', and in each case there is a significant decrease in

crystallite size with freeze/thaw treatment, but at the lower resolvable limit of 50 Å crystallite size the lines are very broad and difficult to measure and only estimates can be given.

6. Discussion

This work has revealed that freezing precipitating gelatinous solids produces a significant decrease in L_c , the crystallite size, although particulate 'clumping' often leads to larger flocs.

Subsidiary effects previously reported, such as structure variations with pH, source, aging and temperature of freezing have been confirmed but confirmation of the dehydration of $Al(OH)_3$, and sludges containing this hydroxide, has been complicated by retained 'capillary' water, which may or may not have been 'squeezed' into the gel or sludge by the increase in pressure due to transition from water to ice. It will be remembered that Foote & Saxton (1915) reported a 'retained capillary water' effect in their work on cryogenic volume dilatometry and suggested that gels contained, free, capillary and combined water contents.

It is appropriate at this stage to consider the mechanism of the freezing process and its effect on precipitating solids and attempt to determine whether the forces involved are sufficient to account for the crystallite size reduction observed, remembering that the tensile strength of ice can have values up to 20 $kg.cm^{-2}$, equivalent to 280 p.s.i., that the compressive strength has been recorded as high as 400 p.s.i. and that shear strengths up to 114 p.s.i. (Dorsey, 1940) have been reported.

At the ice crystal interfaces particulate matter is subjected to shear and compressive stresses and we have seen that these forces are often of sufficient magnitude to reduce crystallite size by a factor of as much as 2.

We know that ice changes in density with pressure and Findlay (1918) in his book on Sir Willard Gibb's phase rule has given the ice-water phase diagram shown in Fig. 20. Of the known varieties of ice it can be seen that all except the familiar ice I are denser than water under the same conditions of temperature and pressure. One consequence of this is that the pressure that is exerted by the freezing of water in a confined space can under no circumstances greatly exceed

2500 $kg.cm^{-2}$ equivalent to 34500 p.s.i., because the bulky ice I cannot exist above this pressure and thus we have an upper limit, over the temperature range 0–20°C, to the pressure which can be developed in a confined space due to the volume expansion of ice.

To appreciate the magnitude of a force equivalent to 34500 p.s.i., which is greater than the tensile strength of cast iron (28000 p.s.i.), consider some recorded affects of water freezing. Ganot, in his treatise on physics (Atkinson, 1898) gives the following:

'The expansive force of ice was strikingly shown by some experiments of Major Williams in Canada Having quite filled a 13 inch iron bomb-shell with water, he firmly closed the touch-hole with an iron plug weighing three pounds and exposed it in this state to the frost. After some time the iron plug was forced out with a loud explosion, and thrown to a distance of 415 feet, and a cylinder of ice 8 inches long issued from the opening. . . .'

Or consider the bursting of steel pipes when water freezes. This bursting pressure can be estimated by the following formula, due to Barlow, given in *Machinery's Handbook* (1959), where

$$P = \frac{2T \times S}{O} \quad (4)$$

and P = bursting pressure, in p.s.i., T = wall thickness, in inches, O = outside diameter of pipe, in inches, S = tensile strength of material, in p.s.i.

Taking a lap-welded steel pipe of tensile strength $S = 50000$ p.s.i. and wall thickness $T = 0.2$ inches, of outside diameter 2 inches, then

$$P = \frac{2 \times 0.2 \times 50000}{2} \\ = 10000 \text{ p.s.i. (bursting pressure)}$$

or $\frac{1}{3}$ less than the upper limit which could be reached by ice I, freezing in a confined space and cooling to $-20^\circ C$.

Consider again the pressure developed and exerted on particles in the centre of a gel or sludge drop, of ideal spherical shape, frozen uniformly from the outside inwards. These drops are observed to fracture or burst at a certain diameter (Murdoch, 1971). Let the drop wall-thickness of the ice at this stage be t such that the outside drop diameter is R and the inside diameter of the hollow centre is r .

Table 5. Crystallite size of various forms of glutinous *Y* sludge

(Observed Bragg angle $28^\circ 75'$)				
State	Object of examination	Line width (mm)	L_c observed (Å)	Reduction factor
<i>Y</i> sludge dried at $50^\circ C$	Normal sediment	2.29	101.9	1.63
As above 'freeze-thawed'	As above	3.74	62.5	
<i>Y</i> sludge dried at $110^\circ C$	Effect of dehydration temperature	4.33	53.8	
As above 'freeze-thawed'	As above	5.12	45.5	1.18

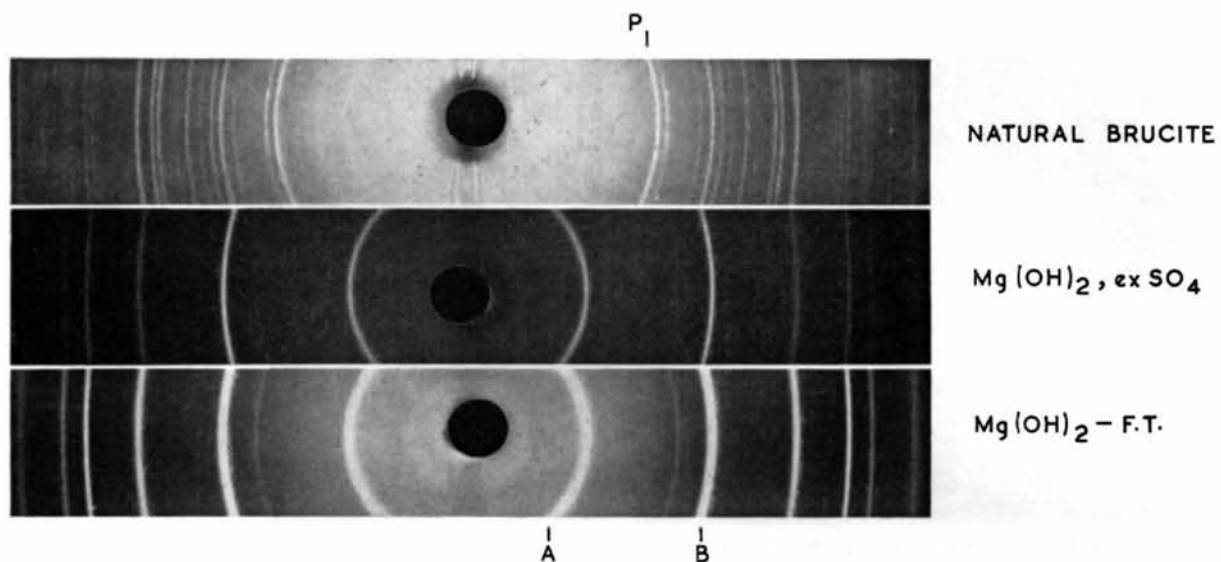


Fig. 7. Powder patterns of natural, precipitated and 'frozen-thawed' magnesium hydroxide

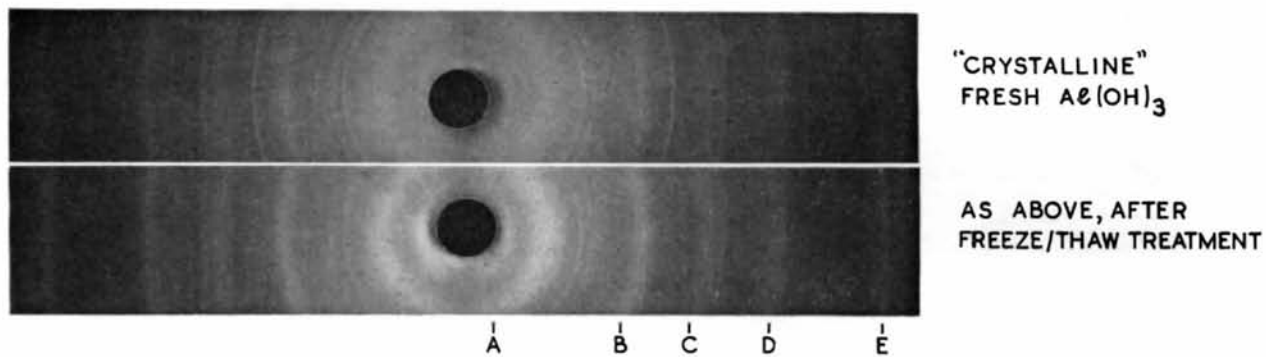


Fig. 9. Line broadening after freeze/thaw treatment

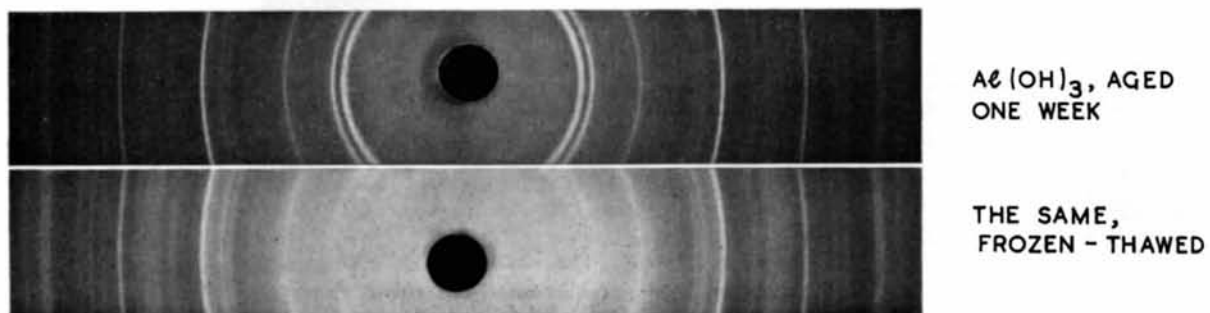


Fig. 10. Effect of time on Al(OH)₃ powder pattern

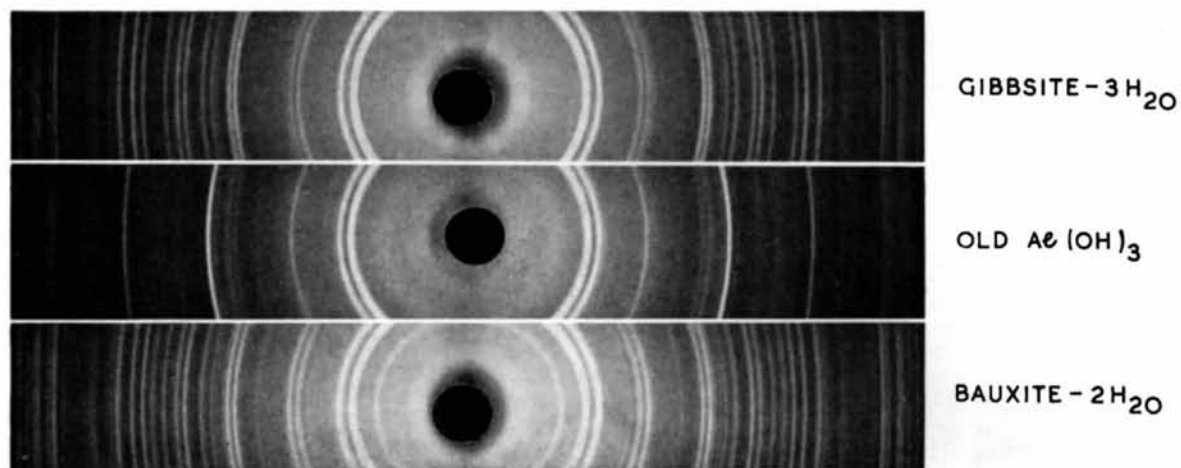


Fig. 11. Comparison between natural oxides of aluminum and aged, precipitated, aluminum hydroxide

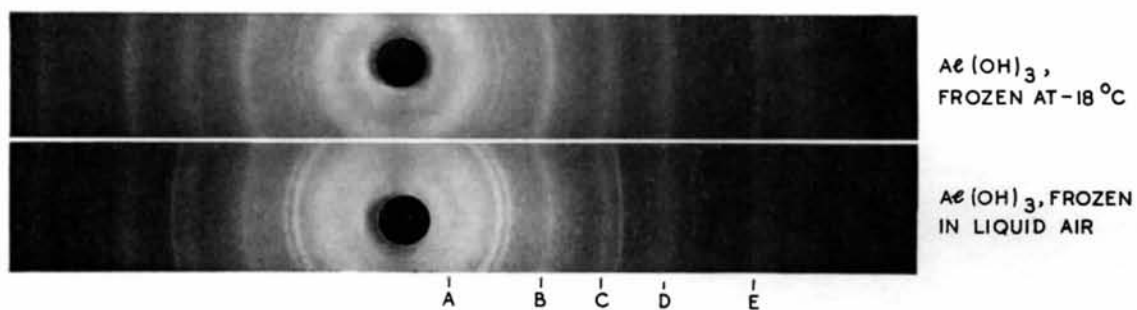


Fig. 12. Effect of freezing temperature on powder pattern of $\text{Al}(\text{OH})_3$

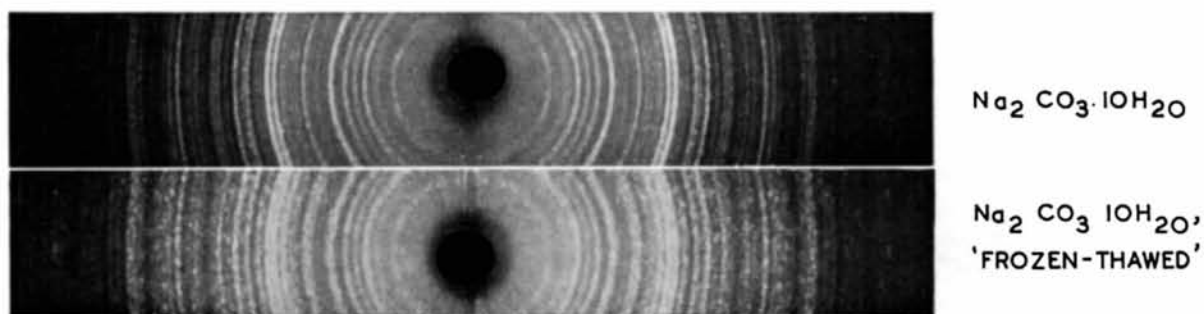


Fig. 13. Sodium carbonate crystals before and after freezing

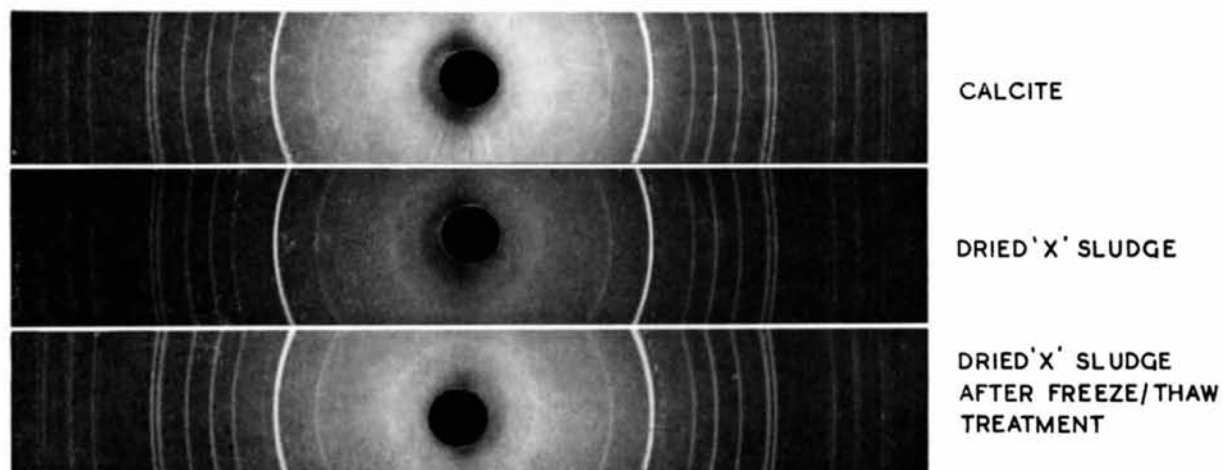


Fig. 16. Water-works *X* sludge, before and after freezing, compared with natural calcite, CaCO_3 .

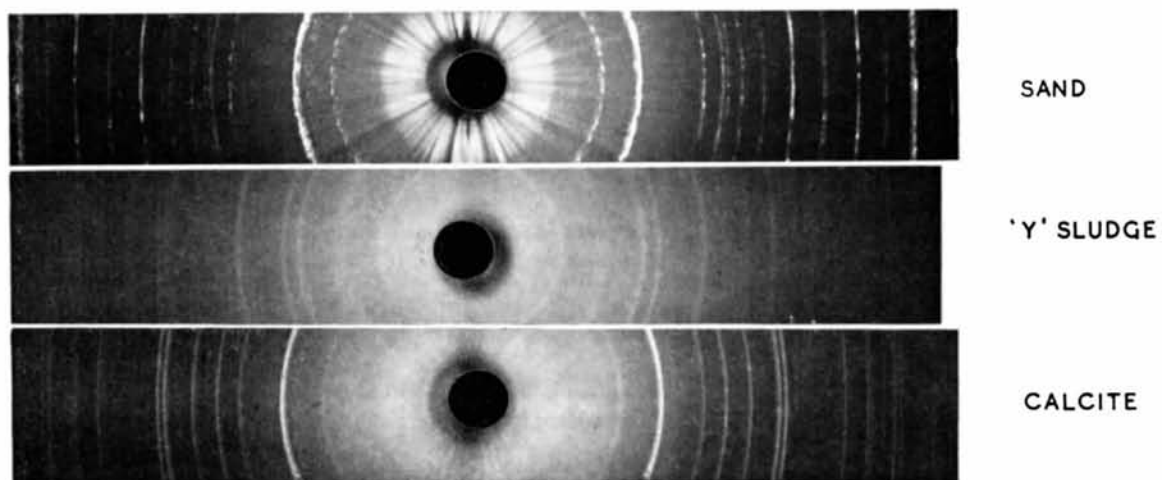


Fig. 17. Viscous *Y* sludge, after drying at 50°C , compared with sand and calcite powder patterns after 8 hr X-ray exposure.

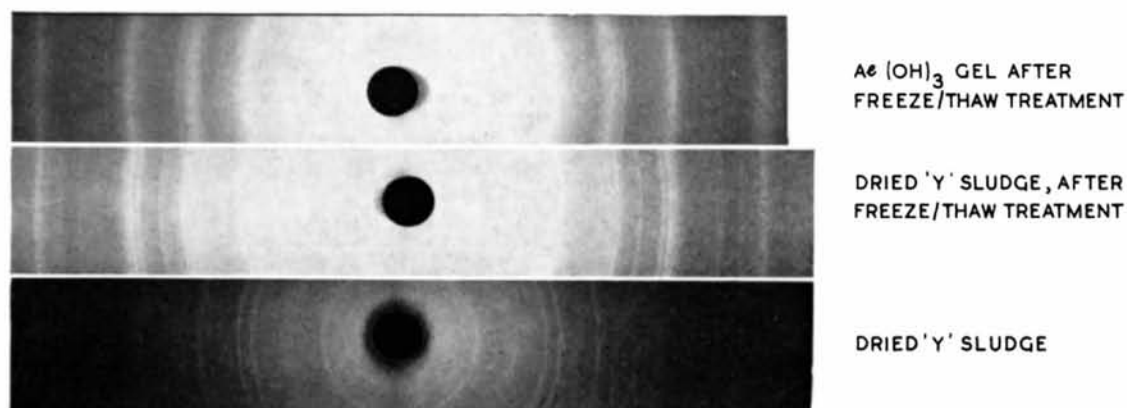


Fig. 18. Resolution of Al(OH)₃ gel component in Y sludge after 12 hr X-ray exposure

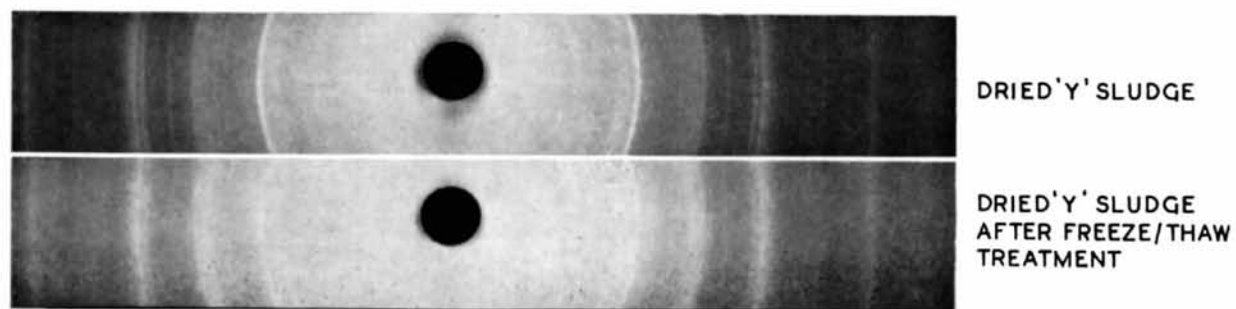


Fig. 19. Resolution of Al(OH)₃ gel component in Y sludge on drying in air at 110°C

Now at the moment of bursting a pressure P will have developed due to volume increase of ice and this pressure per unit area of drop surface inside the hollow centre will be equal to the tensile stress per unit area or tensile strength of ice divided by the rectangular cross-sectional area of drop wall. The internal surface area of the hollow in the drop is $4\pi r^2$,

$$\therefore \frac{P}{4\pi r^2} = \frac{T}{\pi(R^2 - r^2)} \quad (5)$$

$$P = \frac{4r^2 T}{R^2 - r^2} \quad (6)$$

But $R^2 - r^2 = (R+r)(R-r)$ and $R-r=t$:

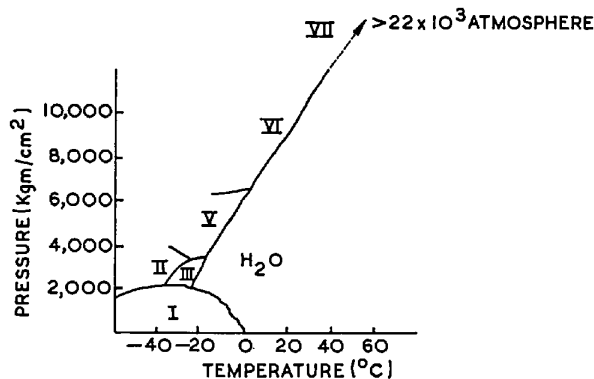
$$\therefore P = \frac{4r^2 T}{t(R+r)} \quad (7)$$

As a numerical case let the dimensions of a frozen drop be:

$$\begin{aligned} \text{outside diameter} &= 0.5 \text{ inches} \\ \therefore R &= 0.25 \text{ inches,} \\ t &= 0.20 \text{ inches} \\ \therefore r = R - t &= 0.25 - 0.20 \text{ inches,} \\ T &= 280 \text{ p.s.i. .} \end{aligned}$$

Then

$$\begin{aligned} P &= \frac{4(0.05)^2 \times 280}{0.2(0.25 + 0.05)} \\ &= 46.7 \text{ p.s.i., the drop bursting pressure.} \end{aligned}$$



ICE VARIETY	DENSITY
I	0.92
II	1.03
III	1.04
IV	?
V	1.09
VI	1.06
VII	

Fig. 20. Pressure/ice-water diagram (Findlay, 1918). Ice densities (Partington, 1931).

Thus if the frozen drop were constrained by other drops on every side, as in a block of frozen sludge, one can see that pressure build-up would be considerable and that partition of particles by failure in shear, their weakest parameter, could well occur. Of course, experimentally, the parameters quoted above would be quite different, but one can begin to see why particle size changes on freezing!

But this is not the whole of the story since we know that the stability of the aluminum hydrates is such that time alone will convert an amorphous gel to a crystalline gibbsite, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, and indeed one method of manufacture of gibbsite is that of aging a suspension of amorphous hydroxide in water (Gitzen, 1970). In addition to this, phase transformation of the aluminum hydrates is very pressure sensitive, as can be seen from Fig. 21, where a pressure lower than 100 p.s.i., at about 120°C , is all that is needed to pass from a gibbsite phase of $\alpha\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ to a boehmite phase of $\beta\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and similar transformations at the lower temperatures and much higher pressures we have been studying in this work, may well be possible.

Having established that gels and sludges are often positively charged before freezing and that after freezing the crystallite size is reduced, one must try to explain why precipitation after a freeze/thaw treatment is so very much faster.

It is thought that the surface charge which a powdered oxide forms in liquid suspension or the charge on the crystallites in a gel determine the extent of flocculation or dispersion and the viscosity of the suspension (Gitzen, 1970). One could suppose, therefore, that the charge on gel or sludge crystallites before freezing is redistributed on very many more particles as the crystallite size has decreased after freezing, as a result of particle fracture in shear, and that the smaller overall charge per particle leads to rapid precipitation.

Alternatively, as a more likely explanation, one might suppose that an appreciable charge loss or neutralization occurs during the phase transformation cycle in the sludge freeze-thaw process, and that the particle size, L_c , has only decreased because of the compressive forces in the frozen state.

Appreciable crystallite charge loss or neutralization may well take place, since the work of Workman & Reynolds (1950) has shown that a large potential sometimes as high as 230 V develops across the ice-water interface in very dilute solutions of the order of $10^{-5}N$ (ammonium hydroxide for example). Gill (1953) confirmed this work and showed that the ice was always positive with respect to the liquid and since the sludge crystallites are found in the liquid between the ice crystals and have been shown to carry a positive charge it would not be surprising if the negatively charged liquid neutralized some of this particle charge during freezing. Some idea of the magnitude of this freezing potential effect is shown in Fig. 22, where the potential across the ice-water front is plotted against freezing time, in a $10^{-5}N$ ammonium hydroxide solution.

The effect is so marked that when dilute potassium permanganate solution is frozen, the positive potassium ions are frozen into the ice, producing a colourless ice in a highly coloured solution due to the residual separated negative manganese ions, with charge transfers of the order of 45,000 e.s.u. per cm^3 of ice formed.

7. Conclusions

It is apparent that the major effects of a freeze/thaw treatment on a viscous or gelatinous sludge or slurry is the observed rapid increase in precipitation and an overall decrease in crystallite size. It is also suggested that the positive charge carried by particles in an aluminum hydroxide gel or in a sludge containing this component is either reduced by dispersion on the many more crystallites, after freezing, or that the freezing process itself partly neutralizes this charge and that the crystallite size is merely reduced by compression.

In view of the marked phase changes which occur as a result of aging of gels, sludges, or slurries, it is recommended that on an industrial scale these materials are never bulk-filtered until at least a week after formation.

The author wishes to thank Mr Burns and Dr J. B. Lewis for their support of this 'fringe area' basic research and Mr R. Murdoch for many discussions. He would also like to thank Messrs Smyth, Stokes and Berryman for their assistance *re.* sludge supplies. Thanks too must go to Mr R. Shepherd, for construction of the X-ray densitometer described.

APPENDIX

The specific resistance to filtration

This unit, 'designed' to quantify the filtration characteristics of sludges and slurries is given by Coackley (1955) as

$$\frac{dV}{d\theta} = \frac{PA^2}{\eta rc(V + V_e)} \quad (8)$$

where

$\frac{dV}{d\theta}$ = rate of filtration, in $\text{cm}^3 \cdot \text{sec}^{-1}$,

P = the pressure of filtration, in $\text{g} \cdot \text{cm}^{-2}$ (this should really be measured in $\text{dynes} \cdot \text{cm}^{-2}$),

A = the area of filtration, in cm^2 ,

η = the viscosity of the filtrate, in poises,

r = the specific resistance of the sludge solids to filtration, in $\text{sec}^2 \cdot \text{g}^{-1}$,

c = the mass of sludge solids per unit volume of filtrate in $\text{g} \cdot \text{cm}^{-3}$,

V = the total volume of the filtrate, in cm^3 ,

and

V_e = the volume of sludge that would deposit a mass of sludge solids per unit area with a resistance equal to that of the filtering medium, in cm^3 .

Integration of equation (8) at constant pressures gives:

$$\frac{\theta}{V} = V \cdot \frac{\eta rc}{2PA} + \frac{V_e \eta rc}{2PA^2} \quad (9)$$

or

$$\frac{\theta}{V} = bV + a. \quad (10)$$

Thus if $\frac{\theta}{V}$ is plotted against V , a straight line of slope

b should be obtained where

$$b = \frac{\eta rc}{2PA^2} \quad (11)$$

or

$$r = \frac{2bPA^2}{\eta c}, \quad (12)$$

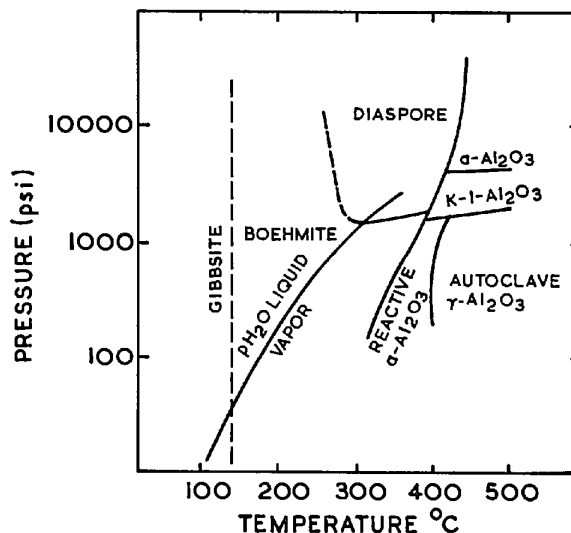


Fig. 21. Pressure sensitive phase transformations in the aluminum hydrates (after Ervin & Osborn, 1951, and Krishna & Torkar, 1962).

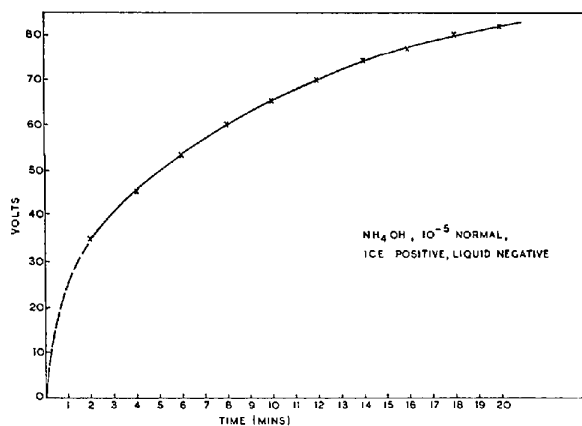


Fig. 22. Rate of growth of freezing potential (after Gill, 1953).

as shown in a paper by Swanwick & Davidson (1961), who reported that the greatest error appeared to be in the value taken for area of filtration A , where an error of 25% in r , the specific resistance to filtration, was recorded. The viscosity η of the filtrate is assumed to be of the order 1, which introduces an error of 7%. Thus Swanwick & Davidson (1961) conclude that if it is assumed that the probable error of a single observation of b is $\pm 2.9\%$, that of A^2 is 25%, and that of η , 5%, then the resulting error in specific resistance is $\pm 25.7\%$.

Such a high order of error is understandable when it is realized that A , the area of filtration, is a function of the geometry of the system, the particle charge, the particle sizes and their distribution and their behaviour under gravity, *etc.* and that therefore this parameter can never be determined with accuracy or reproducibility. Also the value of P , the pressure of filtration, is not a constant, although equation (8) is integrated at constant pressure, since P will vary with precipitate density on filter pad, which again is a function of the variable A . The viscosity, η , of course is not 1 and must vary significantly with the organic content and electrolyte concentration of any sludge.

The mass of sludge solids per unit volume of filtrate, c , is not easy to determine accurately because the water content must vary according to method of filtration, drying conditions and temperature and, of course, density, since water will be retained by capillary attraction. A further factor of some importance would be the age of the sludge, since this leads to increasing granulation and hence better drainage.

V , the total volume of the filtrate, is also a variable because water retention by the sludge is a function of particle size, gel structure, capillary retention, *etc.* and must thus vary from time to time and laboratory to laboratory, as must all the other parameters.

V_e , the volume of the sludge which would deposit a mass of sludge solids per unit area with a resistance equal to that of the filtering medium, is another very ephemeral parameter which is best forgotten as it appears to have been eliminated in equation (12).

Finally we come to r , the specific resistance to filtration. This is a confusing misnomer since its electrical counterpart uses the term specific to imply that electrical resistivity is the reciprocal of conductivity and in the case being examined r only happens to be in reciprocal position in equation (8) and is a unit in its own right, albeit illegitimate!

It is suggested therefore that in sludge and slurry characterization one should revert to simple sedimentation rate measurements and not occupy valuable computer time determining a parameter with such a high degree of error ($\pm 25\%$) and such little absolute meaning.

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