

One advantage of liquid chromatography results from the variety of parameters (selection of column, mobile phase, and temperature) that can be manipulated to produce a desired separation or accelerated elution. In a reverse phase system, the ionic strength of the mobile phase may also be adjusted. Advance knowledge of acid-base or ion-pairing properties of a number of compounds can simplify selection of the optimum ionic strength for their separation.

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TECHNICAL ARTICLES

Effect of Moisture on Tensile Strength of Bulk Solids I: Sodium Chloride and Effect of Particle Size

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Abstract □ The effect of moisture on the tensile strength of packed beds of a variety of particle-size fractions of sodium chloride is reported. At a constant state of packing, the tensile strength of the coarse noncohesive fractions is shown to increase to a plateau as the moisture content rises. This is attributed to an increase in the number and dimension of liquid pendular bonds. For the finer, cohesive fractions, the effect of moisture is initially to cause an increase in tensile strength due possibly to a reduction in interparticle separation as well as pendular bridging. Above a critical moisture content, the tensile strength decreases due to a disruption of the inherent forces of cohesion and the failure to produce new pendular bonds at points of near contact.

Keyphrases □ Tensile strength, bulk solids—effect of moisture on variable particle-size sodium chloride □ Moisture—effect on tensile strength of variable particle-size sodium chloride, bulk solids □ Particle size of bulk solids—effect of moisture on tensile strength

The tensile strength of a powder bed plays an important role in the fundamental theory of shear cell testing (1) and also has been used as an empirical measure of the cohesive properties of the bed (2, 3).

Particle characteristics which influence tensile strength are size distribution (4–12), shape (13), closeness of packing (14, 15), and method of packing (16). In addition, tensile strength is affected by the age of the bed (2), the temperature (17), and the presence of moisture (18–24).

Investigations into the effects of moisture on tensile strength often have been based on ideal models of uniform spheres. Furthermore, there has been a tendency to attribute observed tensile strength changes

Table I—Preparation and Characterization of Size Fractions of Sodium Chloride

Size Fraction, μ	Mean Diameter, μ	Method of Preparation	Shape	
			Elongation Ratio	Description According to British Standard 2955 (1958)
250–353	302 ^a	Sieving	1.06	Crystalline (cubic)
178–250	214 ^a	Sieving	1.06	Crystalline (cubic)
75–178	127 ^a	Sieving	1.19	Crystalline (cubic)
32–75	54 ^a	Sieving	1.50	Angular
<32 μ				
(1)	14 ^b	End-runner milling	1.17	Irregular
(2)	13 ^b	End-runner milling	—	Irregular
(3)	13 ^b	End-runner milling	—	Irregular
<32 μ	5 ^b	Fluid energy milling	1.16	Irregular

^a Mean arithmetic (sieve) diameter. ^b Mass median (Coulter) diameter.

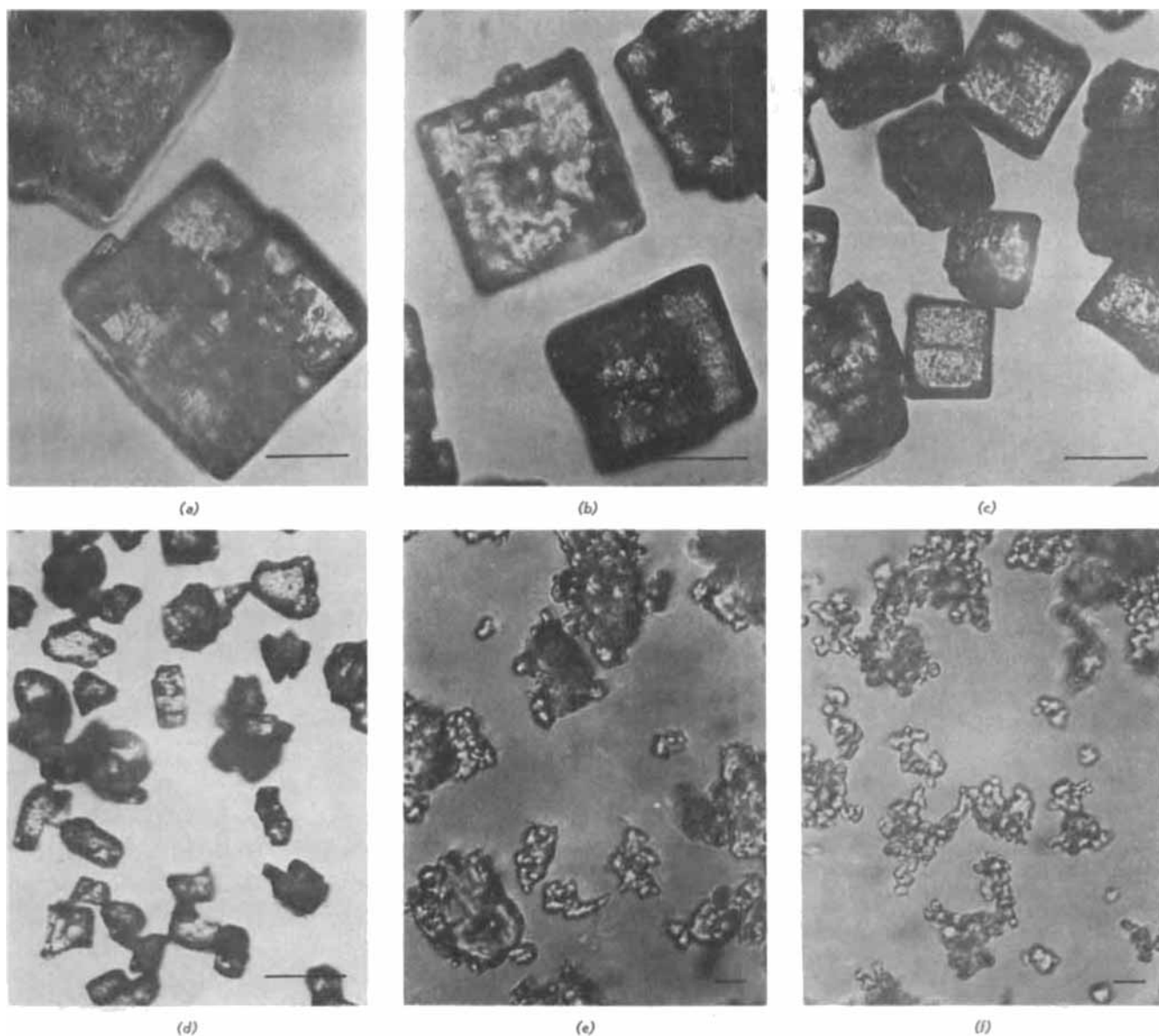


Figure 1—Typical photomicrographs of the size fractions of sodium chloride used. Key: (a), 250–353 μ ; (b), 178–250 μ ; (c), 75–178 μ ; (d), 32–75 μ ; (e), end-runner milled; and (f), micronized. Scale marks: (a), (b), (c), and (d) = 100 μ ; and (e) and (f) = 10 μ .

to one particular underlying mechanism. In this work, a system closer to that encountered in real bulk solids was used, and the effects of moisture on the tensile strength of several size fractions of the material were determined to examine the possibility that the overall effect of moisture may be a result of several mechanisms.

EXPERIMENTAL

Materials—Several size fractions of sodium chloride (Fig. 1 and Table I) were prepared from one purchased batch of BP grade material (particle density 2.15 g. cm.⁻³). Analysis by mass spectrometry for the presence of anticaking agents in the starting material revealed the presence of potassium ferrocyanide, and chemical analysis¹ gave 4 p.p.m. of K₄Fe(CN)₆.

Procedure—Each of the six size fractions was poured into aluminum foil trays, 10.2 cm. (4 in.) by 6.4 cm. (2.5 in.) by 5 mm.

deep, and scraped level. After drying to constant weight at 120°, the trays were transferred to a specially designed and constructed temperature and humidity controlled cabinet (25), previously equilibrated at 28° and below 25% relative humidity (R.H.). When cool, the tensile strengths of the size fractions were determined on each sample, using the apparatus shown diagrammatically in Fig. 2. Samples were prepared for testing by dredging material into the circular cell fitted with the consolidating ring. The loose bed was then compacted by applying weights to the plunger, which was then twisted in a controlled manner. After removing the normal load and consolidating ring, the bed was cut level with the cell rim ready for horizontal stress application. The detailed procedure was reported previously (26).

Higher moisture contents than could be achieved in this way were obtained by: (a) exposing material dried in the trays to relative humidities above 75% until the moisture uptake (accompanied by dissolution) reached the required level, (b) adding a calculated weight of distilled water from a syringe to the samples and distributing the moisture throughout the sample by careful stirring, and (c) adding the required amount of saturated sodium chloride solution at 28° in a similar way.

Some of the end-runner milled material was tested after overnight exposure to 50–59% R.H. and immediately after exposure to 75–79% R.H.

¹ Analar Standards for Laboratory Chemicals, 1967.

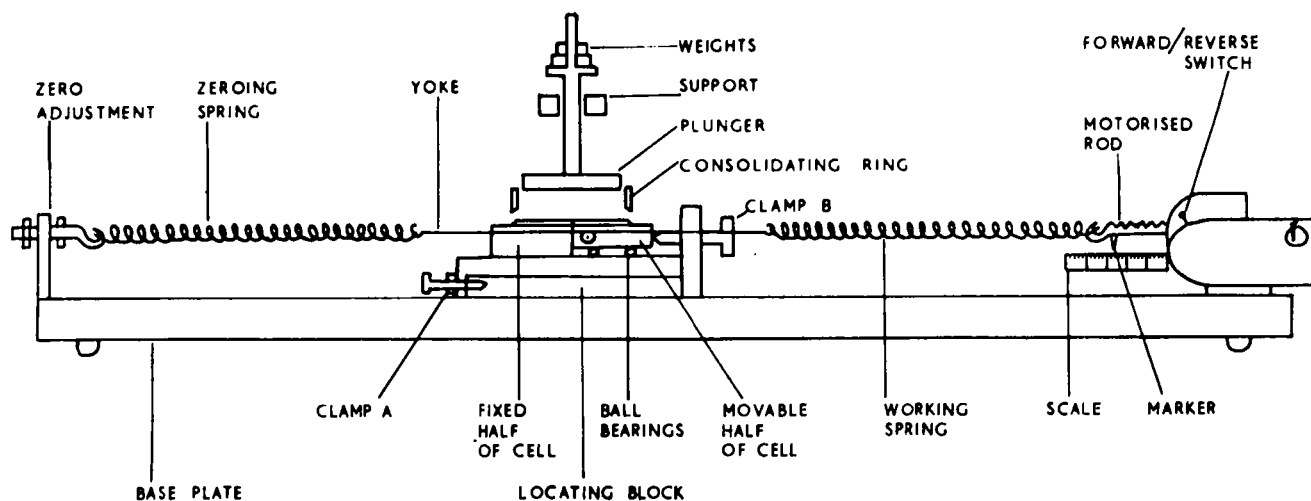


Figure 2—Diagrammatic representation of tensile testing apparatus.

RESULTS AND DISCUSSION

Tensile Strength of Dry Bulk Solids—Figure 3 shows the tensile strengths of the various dry size fractions at different packing densities. In this figure, packing density = ρ_B/ρ_P , where ρ_B = bulk density, and ρ_P = particle density, which may be directly related to porosity, ϵ , as follows:

$$\epsilon = 1 - \rho_B/\rho_P \quad (\text{Eq. 1})$$

Tensile strengths could only be determined satisfactorily when the gravitational forces on the particles were outweighed by the forces of attraction between them. For the fractions studied, therefore, those greater than 75μ could not be tested dry because the material simply drained away as the cell split apart.

Several recent reviews (27–30) considered the nature of interparticle forces. For the bulk solids studied here, the only forces likely to make a noticeable contribution to tensile strength are van der Waals' (molecular) forces and interactions due to mechanical interlocking. Electrostatic forces are considered too small to be significant (28).

Critical particle sizes of other bulk solids below which coherence occurs were reported by Jones (31). For the finer fractions, the tensile strengths increased with packing density (only slightly for the $32\text{--}75\text{-}\mu$ fraction), and this increase may be attributed to an increase in both the number and magnitude of the particle particle interactions.

Changes in coordination number with porosity have been predicted for randomly packed monosize spheres (6, 32, 33); but for real systems of irregular particles, in which more than one point of contact may occur between two adjacent particles, accurate prediction is impossible. Nevertheless, theories of tensile strength have been put forward on the basis of idealized particle systems (6, 12, 34).

The increased tensile strength is likely to be due to an increase in van der Waals' forces produced by the smaller distances of particle separation (35).

The amount of scatter in Fig. 3 is usual for tensile strength determinations [compare Cheng (12), Ashton *et al.* (14), Jimbo *et al.* (16), and Jayasinghe *et al.* (17)] and in this case probably arises from slightly uneven fracture planes.

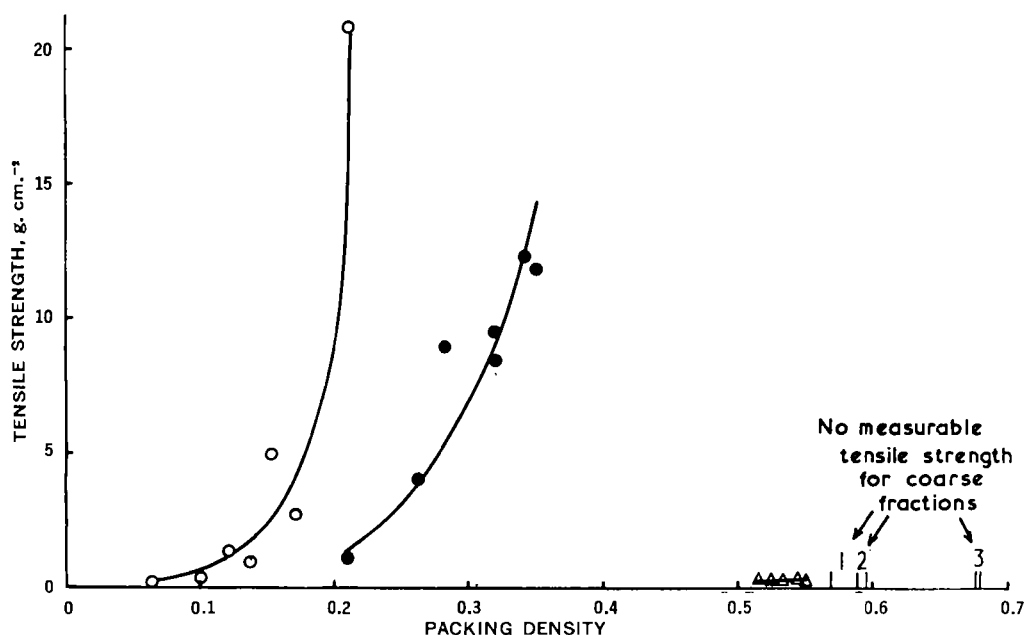


Figure 3—Tensile strength of dry sodium chloride fractions at packing densities produced by consolidating stresses from 2.2 to 101.9 g. cm.⁻². Key: O, micronized (mass median diameter 5 μ); ●, end-runner milled (mass median diameter 14 μ); Δ, 32–75-μ fraction; 1, 250–353-μ fraction; 2, 178–250-μ fraction; and 3, 75–178-μ fraction.

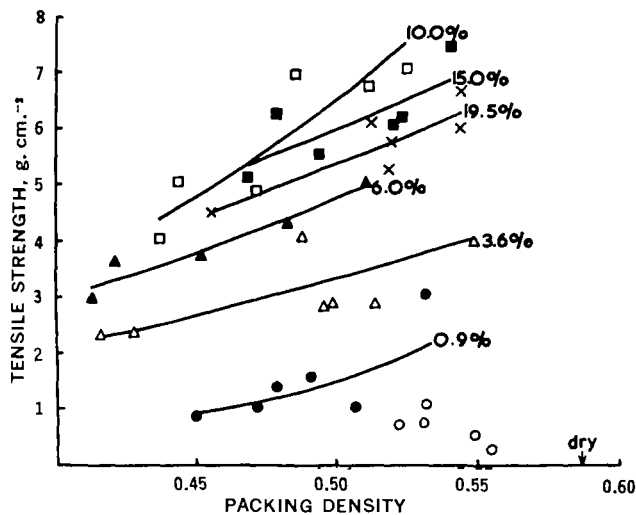


Figure 4—Tensile strengths of sodium chloride, 178–250 μ , at various packing densities (ρ_B/ρ_P) produced by consolidating stresses from 2.2 to 77.0 g. cm.⁻², where ρ_B = weight of undissolved sodium chloride/bed volume, and ρ_P = particle density. Curves shown are taken from double log regression lines. Range of % w/w loss on drying (dry basis) values: \circ , 0–0.3; \bullet , 0.3–1.4; Δ , 3.3–4.0; \blacktriangle , 5.8–6.1; \square , 9.4–10.6; \blacksquare , 14.5–15.4; and \times , 19.1–19.9.

Tensile Strength of Moist Bulk Solids—The effects of moisture on the tensile strength of sodium chloride were found to vary for the different particle-size fractions studied.

Coarse Fractions Greater than 32 μ —For the fractions that, when dry, possess unmeasurable tensile strengths, it was found that the relative humidity had to exceed 75% before the particle-particle interactions increased sufficiently to allow satisfactory determinations. The necessary moisture content, however, was less than 0.1% w/w (dry basis). Typical results for the coarse fractions are shown in Fig. 4. The packing density is calculated from the weight of undissolved sodium chloride (26) and, therefore, retains the same relationship with porosity as for the dry fractions (Eq. 1).

From Fig. 4, it is clear that small percentages of water (0–0.3% w/w) have considerable effects on tensile strength. Within this range, therefore, each determined point probably lies on different tensile strength *versus* packing density curves, which cannot be fully elucidated because of the continuous increase in moisture content. At higher moisture contents, however, the effects are less pronounced and it can be assumed that all the points determined within a narrow range of moisture contents lie on the same curve, which is representative of the average moisture content.

The position of the curve was determined by plotting the double log regression line by the method of least squares using a KDF 9 computer. By reading off values of tensile strength at fixed values of packing density and plotting these against the moisture content, curves such as those in Fig. 5 for the 75–178- μ fraction are obtained.

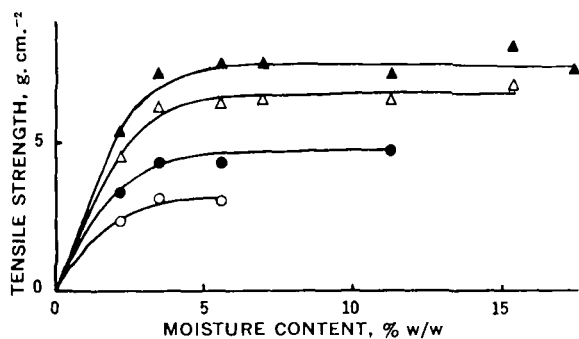


Figure 5—Effect of moisture content (% w/w, dry basis) on the tensile strength of sodium chloride, 75–178 μ , at various packing densities calculated on the basis of the weight of undissolved solid only. Packing density: \circ , 0.398; \bullet , 0.437; Δ , 0.479; and \blacktriangle , 0.501.

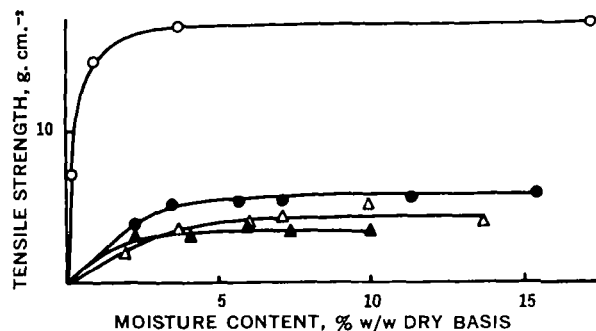


Figure 6—Tensile strength of coarse sodium chloride fractions at various moisture contents at a packing density of 0.457. Size fraction: \circ , 32–75 μ ; \bullet , 75–178 μ ; Δ , 178–250 μ ; and \blacktriangle , 250–353 μ . Points are taken from regression lines of $\log T$ versus $\log \rho_B/\rho_P$.

It can be seen that as the moisture content increases, the tensile strength at a fixed packing density increases to a plateau. This plateau may not be evident, however, if the packing density is expressed on the basis of the total weight of sodium chloride (dissolved and undissolved) and water (36).

Curves for each of the four coarse fractions greater than 32 μ at a fixed packing density are shown in Fig. 6. The tensile strengths of each fraction increase with moisture content up to about 4% w/w (dry basis) and thereafter remain reasonably constant. In addition, the tensile strengths at any moisture content increase with a decrease in particle size.

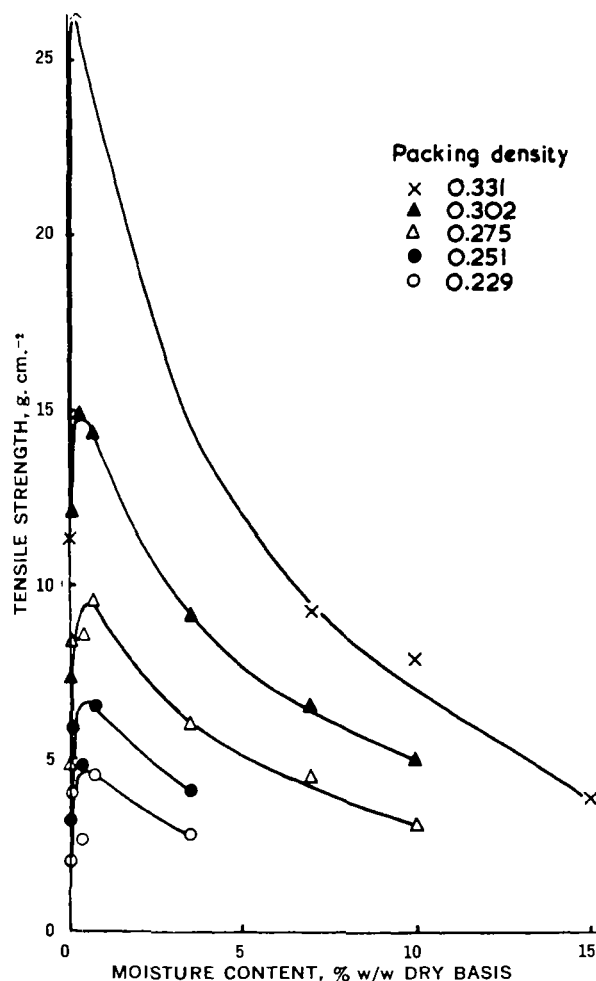


Figure 7—Tensile strength of end-runner milled sodium chloride Baich 1 (mass median diameter 14 μ) at various moisture contents achieved by exposure to various relative humidities.

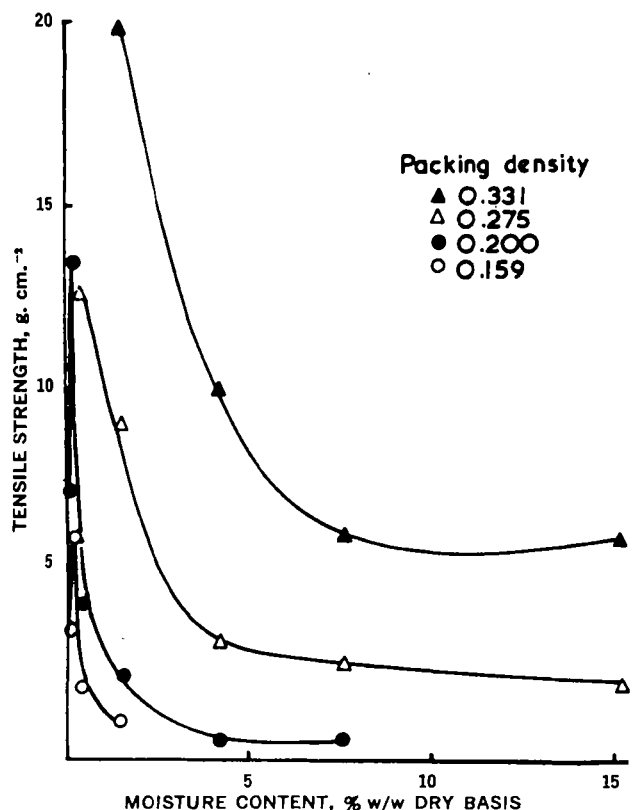


Figure 8—Tensile strength of micronized sodium chloride (mass medium diameter 5 μ) at various moisture contents achieved by the addition of saturated sodium chloride solution.

The increase in tensile strength of the coarse fractions to measurable values at moisture contents of below 0.1% w/w (dry basis) may be attributed to the production of pendular bonds (18). The existence of these liquid bridges brings the coarse fractions (free flowing when dry) into the cohesive category, and the curves showing the increase in tensile strength with packing density (Fig. 4) are comparable with the ones for the dry cohesive fractions less than 32 μ (Fig. 3). The sizes and distribution of pendular bonds in beds of regular-shaped particles were discussed by Fowler and Radford (19), Carr (8), and Clark and Mason (37). It is clear that they are dependent on whether the system is wetted before or after bed preparation. If before, the method of bed preparation is also important; if after, achieving the required moisture content by raising it from dryness may produce different sizes and distributions of pendular bonds from reducing it (by drying) from a higher level.

In this work the coarse fractions were exposed to high relative humidities until the moisture content reached the required level and then the bed was prepared in a standard way. At a fixed packing density, therefore, the following two changes may be expected with increasing moisture content: (a) an increase in the number of pendular bonds, first at points of contact and later, at higher moisture contents, at suitable points of near contact, and (b) an increase in the dimensions of these pendular bonds.

Fisher (38) showed the attractive force F due to a pendular bond between two equal touching spheres to be:

$$F = \frac{2\pi r\alpha}{1 + \tan^{1/2}\theta} \quad (\text{Eq. 2})$$

where r = radius of spheres, α = surface tension of liquid, and θ = half the angle subtended at the center of each sphere by the lens of water.

It can be seen that as the liquid bridge increases in size, the attractive force decreases. Pietsch and Rumpf (21), however, showed that if equal spheres were separated by at least $1/100$ of the sphere diameter, an increase in the size of the liquid bridges produced an increase in the attractive forces, but at any percentage liquid saturation the touching spheres yielded the greatest force. Clark and Mason (37) suggested a linear decrease of the force with sphere

separation from a maximum at contact to zero when rupture occurred.

Although the coarse fractions of sodium chloride did not consist of ideal spheres, it may be expected that liquid bridges would form at the tips of surface projections where conditions would approximate the theoretical cases discussed. For instance, the increase in tensile strength of the coarse fractions up to 4% w/w (dry basis) moisture (Fig. 6) may be attributed to the production of pendular bonds at points of contact and of near contact and the increase in size of the latter. However, at 4% all available sites for pendular bonds may be taken and the tensile strength remains constant due to a balance between the increasing forces at the points of near contact and the decreasing forces at points of actual contact.

The effects of particle size (Fig. 6) may similarly be explained since, at a fixed packing density, finer particles would produce more potential sites for pendular bonds, in a given cross section of the bed, than coarse particles.

Fine Fractions Less than 32 μ —The effects of moisture on the tensile strength of the fine fractions of sodium chloride at fixed packing densities were analyzed in the same way as for the coarse fractions. Figure 7 shows typical results for the end-runner milled material. Small increases in moisture content, produced by adsorption at relative humidities below 75%, produced large increases in

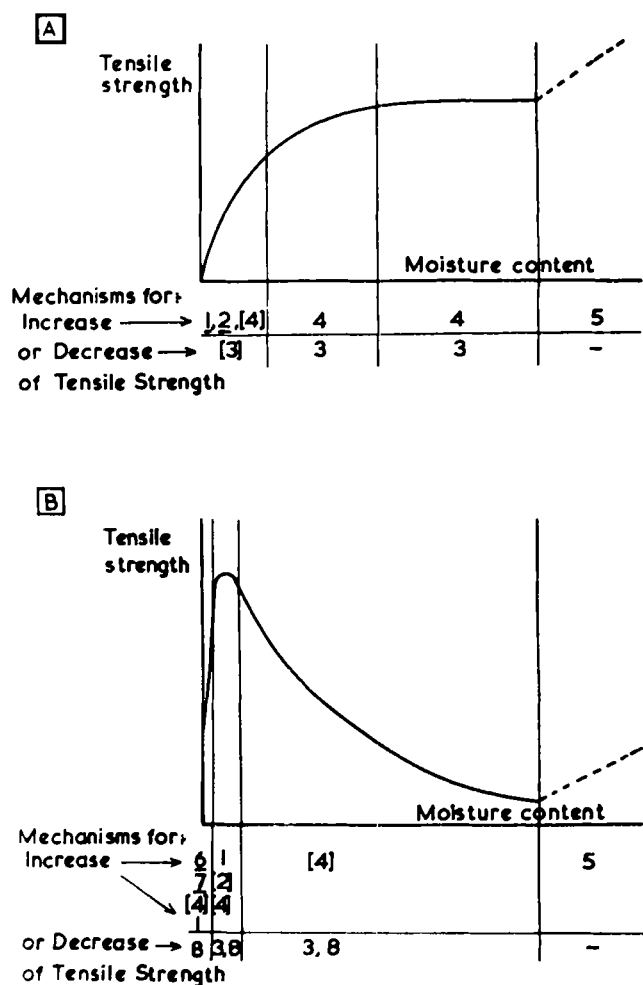


Figure 9—Summary of probable explanations of changes in tensile strength with moisture content for typical fractions of sodium chloride. A = greater than 32 μ ; B = smaller than 32 μ . Key: 1, new pendular bonds form at points of contact; 2, pendular bonds form at points of near contact; 3, pendular bonds at points of contact increase in dimensions; 4, pendular bonds at points of near contact increase in dimensions; 5, pendular bonds unite (i.e., funicular state approached); 6, small surface irregularities smoothed out and area of contact increased; 7, interparticle distance effectively reduced; and 8, disruption of cohesive forces inherent at dryness. Minor effects are bracketed; major effects are underlined.

tensile strength, but these were followed by a subsequent decrease to values below those at dryness.

The micronized sample showed similar effects (Fig. 8) but possessed a higher tensile strength below approximately 0.3% w/w moisture (dry basis). As the moisture content increased, the tensile strength decreased to less than the coarse end-runner milled samples.

The increases in tensile strength produced by small amounts of adsorbed moisture (Figs. 7 and 8) may be attributed to one or more of the following effects of moisture:

1. It may smooth out surface microirregularities and thus increase the area of contact.

2. It may effectively reduce the interparticle separation and thus increase van der Waals' forces (5).

3. It may produce pendular bonds. For instance, Rumpf (6) stated that water formed liquid menisci in capillaries with radii greater than 30 Å. It is likely, therefore, that adsorbed layers greater than 30 Å thick may yield normal surface-tension values. The total thickness of adsorbed water layers may be estimated as follows:

$$\text{thickness (Å)} = \frac{5.6Nb}{18S \times 10^{21}} \quad (\text{Eq. 3})$$

where N = Avogadro's number, b = percentage moisture content (dry basis), and S = specific surface ($\text{m}^2 \text{g}^{-1}$). This assumes: (a) the cross-sectional area of an adsorbed water molecule to be 14.1 Å^2 [calculated from the density of liquid by the method of Emmett and Brunauer (39)], and (b) the thickness of each adsorbed layer to be 4 Å.

For the end-runner milled material, Sample 1 (specific surface $0.7 \text{ m}^2 \text{g}^{-1}$, determined by means of Ströhlein nitrogen adsorption apparatus), the moisture content [approximately 0.1% w/w, dry basis achieved by adsorption at 64–68% R.H. (Fig. 7)] can be shown to represent a thickness of about 27 Å. Since this thickness is approaching that at which normal surface-tension values may be anticipated (i.e., 30 Å), it is possible that pendular bond production may contribute to the initial increases in tensile strength shown in Figs. 7 and 8. This is substantiated by the fact that the samples of end-runner milled material yielded similar moisture contents and comparable tensile strengths whether they were stored overnight at 50–59% R.H. or introduced into an atmosphere exceeding 75% (at which they began to deliquesce) and tested immediately.

Possible explanations of the decrease in tensile strength of beds of the fine fractions at moisture contents in excess of about 0.5% by weight (dry basis) are as follows:

1. The inherent forces of cohesion present in the dry material may be disrupted. For instance, mechanical interactions may be reduced by lubrication (40) or van der Waals' forces by the presence of liquid bridges.

This effect is almost certainly involved since the particle-particle interactions responsible for the inherent tensile strength at dryness occur at the same positions as those where moisture collects, namely, the points of contact. Furthermore, the reduction cannot be attributed to changes in particle size or shape brought about by dissolution since similar effects are obtained whether water or saturated sodium chloride solution is added.

2. The failure to produce new pendular bonds at points of near contact with an increase of moisture content results in the growth of existing bridges (at points of actual contact) and the corresponding reduction in the force of attraction.

This is also a likely explanation since the packing densities of the fine fractions (Figs. 7 and 8) are much lower than for the coarse materials (Figs. 4 and 5), and one might therefore expect fewer points of near contact capable of producing new liquid bridges.

3. The aggregation of the fine particles produce an effectively greater particle size.

This is less likely because the aggregation would be apparent during testing and significant changes in the appearance of the fracture would be observed.

CONCLUSION

The most likely effects of moisture, both for the coarse and fine fractions, are summarized in Fig. 9. It may be seen that the different effects obtained may be due either to the fine fractions producing fewer new pendular bonds at points of near contact or to the disruption of the cohesive forces present in the dry fine materials. Thus, the factors responsible for the different effects may not necessarily be particle size but the associated magnitude of the coherence of the

material when dry. Investigations into these aspects will be reported in a subsequent publication.

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