

Moisture uptake and tensile strength of bulk solids

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An apparatus is described in which bulk solid handling properties can be examined over a wide range of humidities. It is shown that constant temperature and relative humidity can be maintained. The apparatus can also be used to study the effect of cycles of humidity changes. The rate of moisture uptake by loosely packed and tapped beds of six pharmaceutical materials was found to be dependent upon bed depth but independent of bulk density. The tensile strengths of the bulk solids changed when they were subjected to high relative humidities.

The presence of moisture in bulk solids can seriously impair the flow properties of materials and thus cause non-uniform dosage in preparations or loss of efficiency in processing. It may, however, be used to advantage in granulation.

The strengths of powder beds containing excess moisture have been measured using a tilting table split plate apparatus (Eisner, Fogg & Taylor, 1960; Shotton & Harb, 1966). More recently, measurements of the strength of moist agglomerates and compressed beds of bulk solids have shown that significant changes in tensile strength can occur according to the physical location of moisture within the specimens (Rumpf, 1958; Smalley & Smalley, 1964; Pietsch, 1967; 1968; Pietsch, Hoffman & Rumpf, 1969); Griffiths (1969) has reviewed the effects of moisture in tablet manufacture.

The application of shear and tensile strength determination to problems of bulk solid flow behaviour permits a complete description of powder behaviour in terms of certain derived parameters (Jenike, 1961; Williams, 1965; Farley & Valentin, 1967–68). These investigations show that particle size, size distribution and shape affect the cohesion and tensile strength of bulk solids (Cheng, 1968) but in all cases the moisture content was not varied.

It would therefore be desirable to investigate the changes in tensile strength that occur when a dry bulk solid is exposed to a humid environment.

It is not convenient to use conventional humidity cabinets for this purpose since transference from high relative humidities to measuring apparatus in laboratory environments leads to severe errors due to loss of moisture by evaporation and desorption. Therefore an apparatus was constructed so that all measurement could be made within a controlled environment.

The tensile strength of bulk solids at different humidities depends, amongst other variables, on the rate of moisture uptake and loss by the powder bed. This, in turn, may be expected to vary with the state of packing and depth of the beds.

Furthermore, caking may occur with some material when moisture is lost. Consequently the apparatus was designed to examine the effects of cyclic variations in humidity. In the first instance, a range of materials of pharmaceutical interest has been studied to indicate the gross effects that may occur.

steel. This floor consists of a series of trays perforated at regular intervals with $\frac{1}{2}$ inch diameter holes. The tray nearest the inlet port is only partially drilled to prevent channelling of the inlet air before dispersal.

After passing up the chamber, the air leaves via a central ceiling orifice baffled as a further prevention against channelling.

The temperature of the chamber and the air is maintained constant by an adjustable mercury contact thermometer, T_1 , situated in the centre compartment (i.e. the one which is always in use). This controls a 200 W mica "black body" heating element h_1 mounted together with a similar but manually operated heater h_2 for initial warming up. Details of the electrical controls are presented in Fig. 2.

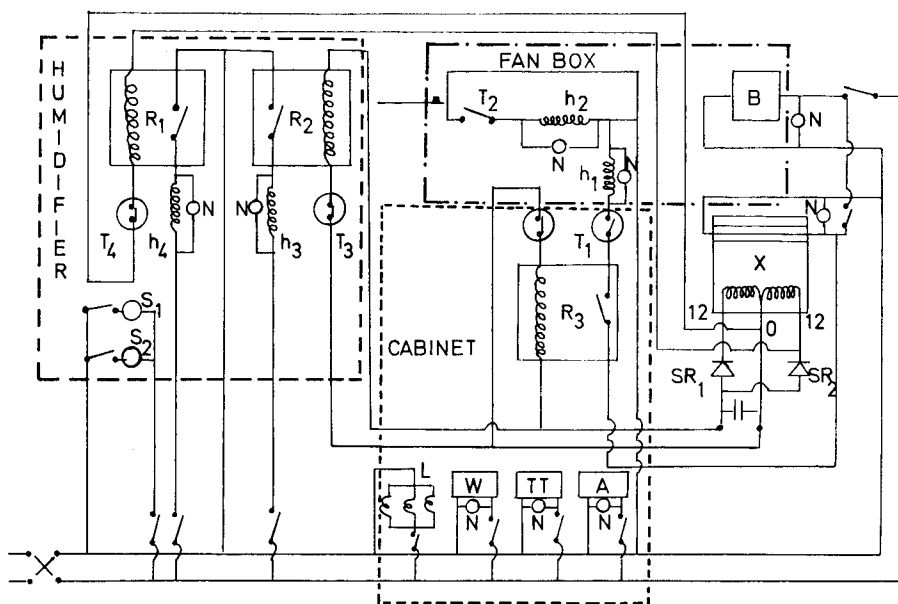


FIG. 2. Circuit diagram of controlled temperature and humidity chamber. Symbols as Fig. 1 plus A, hygrometer; L, lights; N, indicating neons; R_1 - R_3 , relays; SR_1 SR_2 , silicon rectifiers; TT, tensile tester; W, balance; X, transformer.

These heaters are situated in a chamber, B, containing a centrifugal blower (1/30 H.P. shaded pole, ventilated motor with $4\frac{5}{8}$ inch diameter $2\frac{3}{8}$ inch width impeller operating at 2500 rev/min) and excess temperature rises during boost heating are controlled by a bimetallic strip thermostat, T_2 , set to open at 70° . This thermostat, which is wired in series with the main and boost heaters, enables the apparatus to be left unattended with safety in case of instrument failure.

Constant humidity is achieved by circulating the air over magnetically stirred saturated salt solutions, S_1 S_2 , containing excess undissolved salt. The humidifiers, H_1 H_2 , are designed to profile the air flow such that a large evaporative surface is presented to a narrow jet of air.

Establishment of the desired relative humidity may be prolonged if the latent heat of evaporation is not externally supplied since the solutions will remove sensible heat from the circulating air (Garton, 1948). The solutions in the humidifier trays

are therefore maintained at a constant temperature by 100 W pencil-type immersion heaters h_3 , h_4 controlled by narrow range adjustable mercury contact thermometers T_3 , T_4 .

Choice of the salt solution is made by reference to the literature (Wexler, 1965; Young, 1967) from which it can be seen that relative humidities over the range 20–90% may be obtained. Precise adjustment of relative humidity is possible by accurate control of the temperature of the saturated salt solutions.

Using different salt solutions in each humidifier consecutively, changes in relative humidity can be effected, thus permitting a cycle of changes to be made. Reduction in humidity can be rapidly produced by the use of desiccants.

All connections of air supply are by 2 inch diameter plastic flexible hosing and 1½ inch diameter polypropylene manifolds. The air flow rate is measured by using a suspended float-type flow meter, F (range 20–200 litre air/min at 15° and 760 mm Hg) and is controlled by precision unplasticized PVC gate or aluminium butterfly valves. Pressure within the circuit is monitored from the centre compartment by means of a U-tube manometer.

Heat losses are kept minimal by the liberal use of expanded polystyrene and hair felt lagging.

Results of apparatus behaviour

Some common causes of error during the maintenance of atmospheres of known temperature and humidity are listed by Garton (1948). These include the non-uniformity of temperature and partial water vapour pressure, the latter usually arising from condensation, inadequate air mixing or leakage from the enclosure, or both.

The apparatus described above is designed to minimize these problems and has been used successfully at temperatures between 22° and 28°. However, to avoid the influence of high laboratory temperatures, a working temperature of 28° was chosen. All subsequent reference to relative humidity values, therefore, applies to this temperature.

Starting at an ambient temperature of 23° the air reached working temperature within 1 h. Subsequently, 24 h was allowed as a cabinet temperature equilibration period. By careful adjustment of the inlet valves a temperature of $\pm 0.5^\circ$ throughout the chamber was obtained.

The lagging proved efficient against temperature fluctuation and only minute condensation on the Perspex front plates was evident at relative humidities approaching saturation.

By inserting the flowmeter at strategic positions in the circuit and closing selected valves the presence of leaks could be detected and corrected.

Investigation of the air flow rates with different compartments sealed off showed that the chamber atmosphere was completely changed at least once every 2 min, varying from 1.2 min for a complete air change of the centre compartment only to 1.9 min for all three compartments. Times much below these would lead to problems of dispersal of powder specimens in the apparatus.

Fig. 3 shows the humidification of the chambers using potassium chloride as the salt in both humidifiers. From this it can be seen that satisfactory equilibrium conditions of relative humidity were achieved in less than 1 h. Similar results were

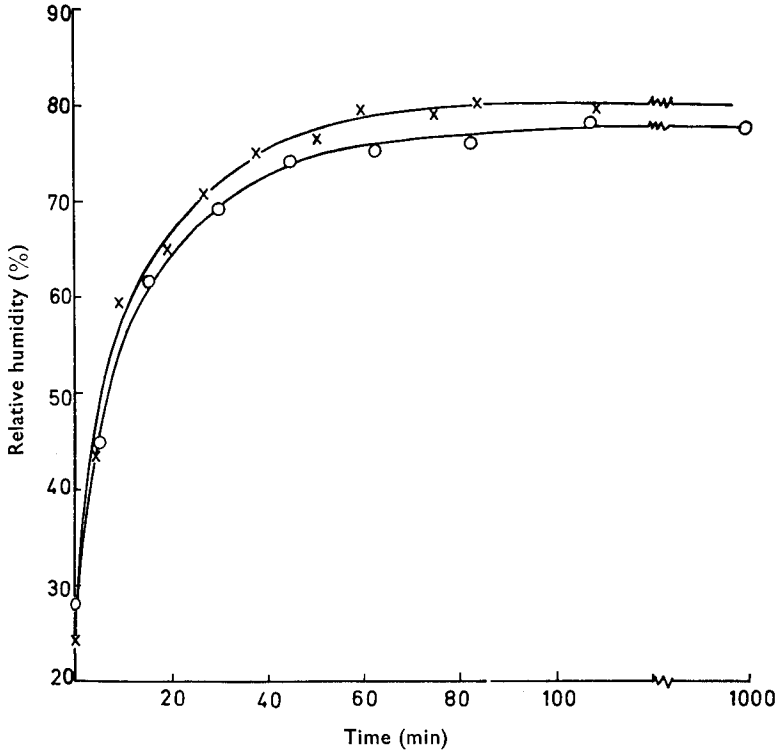


FIG. 3. Humidification of the chamber using saturated potassium chloride solution. ○ two humidifiers $T_1, 28^\circ T_3, T_4, 29^\circ$ × one humidifier $T_1, 28^\circ T_3, 30.5^\circ$ C.

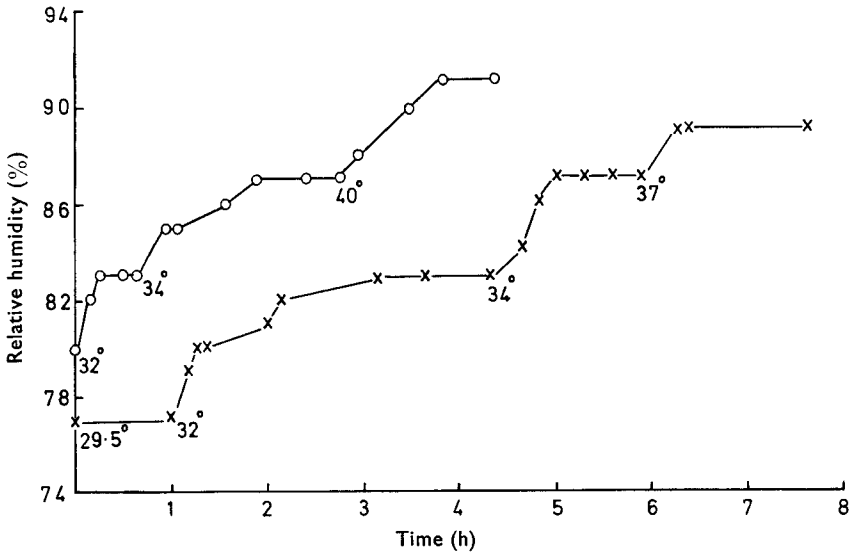


FIG. 4. Fine control of relative humidity by variation of humidifier temperature. Temperature of T_3 adjusted at points indicated. Initial T_3 temperature ○, 32° ; ×, 29.5° .

obtained using other salt solutions giving relative humidities of 28% with potassium acetate and 80% with ammonium dihydrogen orthophosphate and relative humidity variation throughout the working area was found to be $\pm 1.5\%$.

The variation in relative humidity that was produced on controlled increase of the temperature of the humidifier solution is shown in Fig. 4. An increase of 2-4% was achieved by a 2 or 3° change in temperature. Any particular relative humidity obtained in this way could be maintained with the same accuracy as shown above.

All these humidity changes were followed by means of an aspirated wet and dry bulb thermometer of the Assmann type (accuracy $\pm 1\%$ RH) and continuously monitored using a recording human hair thermohygrograph (accuracy $\pm 5\%$ RH). Temperature constancy was checked by means of 15 mercury-in-glass thermometers.

Reduction in humidity was achieved by the use of 500 g of dried coarse silica gel in each humidifier to 10% relative humidity, below which phosphorous pentoxide impregnated onto an inert matrix proved effective. Table 1 shows that the rate of

Table 1. *Effect of time previously spent at elevated relative humidities on subsequent dehumidification process*

Time previously spent at elevated relative humidity	Dehumidification produced by 500 g dried silica gel in each humidifier in the first h	Subsequent time required for RH to reach 14% (silica gel replaced every 6 h)
1 h at 80%	80% to 28%	—
42 h at 78-91%	78% to 66%	12 h
89 h at 76-89%	77% to 66%	20 h

fall in humidity is determined by the length of time over which the high relative humidity had been previously maintained. This is due to adsorbent and absorbent effects associated with the plastic connection hoses which increased the moisture load of the system. At a cabinet relative humidity of 80% and a laboratory relative humidity of 51%, opening the isolated end compartment, by removing a glove for 10 min, was found to lower the relative humidity by 3% when all three compartments were re-connected to circulating air. Complete recovery to equilibrium relative humidity was achieved after 45 min. Removal of a Perspex front for 5 min produced a similar fall requiring 1 h for complete recovery.

Table 2. *Physical characteristics of materials used*

Material	Shape (Elongation ratio)	Particle density g ml ⁻¹ 25°		Bulk density *g ml ⁻¹		
		Immersion fluid	Liquid paraffin	Poured	Tapped	
Calcium phosphate	..	1.51	3.00	2.91	0.29	0.46
Lactose	1.82	1.55	1.55	0.65	0.80
Potato starch	1.25	1.51	1.51	0.40	0.58
Sodium chloride	1.09	2.16	2.14	1.21	1.36
Potassium chloride	1.22	1.96	1.97	1.10	1.21
Sucrose	1.15	1.59	1.59	0.87	1.00

* Bulk densities determined using British Standard (1948) method.

Investigation of bulk solid properties—Materials and Methods

Six bulk solids, differing in both physical and chemical properties, were sampled by chute splitting and dried in thin layers, before investigation, by heating at controlled temperatures in a hot oven for 48 h. The samples were transferred directly to the apparatus maintained at a relative humidity below 25% before humidification. The characteristics of the samples are presented in Tables 2 and 3.

Table 3. *Size characteristics of materials used*

Material	Size distribution				
	Cumulative percentage greater than stated size * Volume surface diameter (μm)				
	80	60	40	20	10
Calcium phosphate ..	—	2	7	22	50
Lactose	2	4	29	69	90
Potato starch	2	15	60	97	99
		Size range†		Arithmetic mean sieve diameter (μm)	
Sodium chloride ..		178–250		214	
Potassium chloride ..		125–250		187	
Sucrose		500–699		600	

* Determined using Coulter Counter Model B.

† Prepared by sieving.

In order to investigate some of the factors influencing moisture uptake, representative samples of the bulk solids were packed into Petri dishes and beakers having internal diameters of approximately 50 mm. The beds were prepared by dredging and tapping such that variations in bed depth and bulk density were obtained. Once prepared these samples were left undisturbed during the subsequent humidification period. Material to be used later for tensile strength determinations was exposed in thinly dredged layers on $4 \times 2\frac{1}{2} \times \frac{1}{2}$ inch aluminium foil trays. Preliminary work had shown that provided the bed depth was of only a few particles thick, moisture distribution throughout the beds was reasonably uniform. As an additional safeguard, material reserved for tensile strength determinations was periodically disturbed by stirring. The apparatus used to determine tensile strength consisted of a horizontal split cell unit similar to that described by Ashton, Farley & Valentin (1964) and the beds were tested immediately after packing into the cell.

Weight increases were determined using a top pan balance (readability 0.001 g precision 0.0005 g) and subsequently checked by determining the weight loss on drying at temperatures which caused no chemical breakdown of the material. These temperatures were selected by reference to thermogravimetric analyses on humidified samples and the results expressed as % weight increase-dry basis.

During the experiments the only attention that the cabinet required was maintenance of the volume of the saturated solutions every two or three days.

RESULTS

Fig. 5 illustrates the effect of bed depth on the weight increase of potato starch, packed to a similar initial bulk density, when exposed to a relative humidity of 85%. It can be seen that the initial establishment of equilibrium humidity conditions is

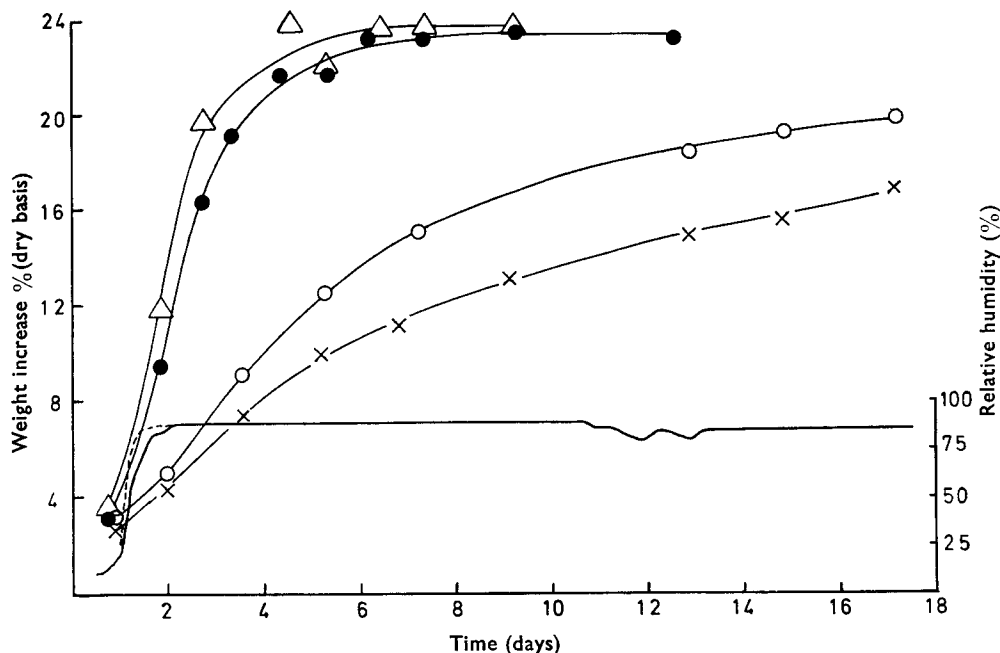


FIG. 5. The effect of bed depth on the moisture uptake of potato starch at similar initial bulk densities. Bulk densities (g ml^{-1}) $\times 0.918$; \circ , 0.946; \bullet , 0.990; \triangle , 0.95. Bed depths (cm) $\times 4.5$. \circ , 2.8; \bullet , 1.2; \triangle , 0.55. Broken line—Cabinet humidification without material present.

retarded. This is due to the excess of material (2 kg) present during testing. It is clear, however, that bed depth significantly influences the uptake of moisture and that equilibrium moisture contents were achieved in a reasonably short period only when thin beds of bulk solid were used.

Similar curves were obtained for lactose and calcium phosphate but in these cases the relative humidity achieved equilibrium in a much shorter time. Equilibrium

Table 4. *Equilibrium moisture contents (EMC) at elevated relative humidities*

Material	Equilibrium R.H.	Total No. of Samples	Mean EMC % w/w loss on drying dry basis	Standard deviation
Calcium phosphate ..	87%	10	1.79	0.08
Lactose	89%	11	5.27	0.17
Potato starch ..	85%	14	23.24	0.40

moisture contents are presented in Table 4. The increase in weight during humidification shown in Fig. 5 was not observed with alkali halides and sucrose. Fig. 6, which shows the effect produced when sodium chloride is humidified, indicates that weight increase occurs only above certain critical relative humidities. Again, the effect of bed depth is evident but in these cases no equilibrium moisture content is reached. The results for potassium chloride and sucrose were similar.

Only small variations in weight increase were observed at different states of packing. Fig. 7 shows typical results for filled containers at low bed depth. The

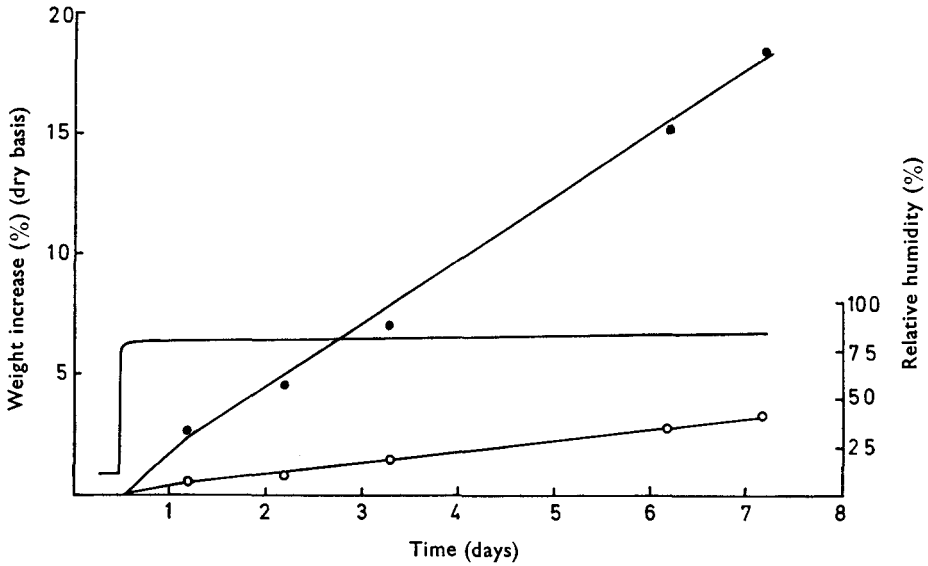


FIG. 6. The effect of bed depth on the moisture uptake of sodium chloride at similar initial bulk densities. Bulk densities (g ml^{-1}) ○, 1.213; ●, 1.260. Bed depth (cm) ○, 2.3; ●, 1.2.

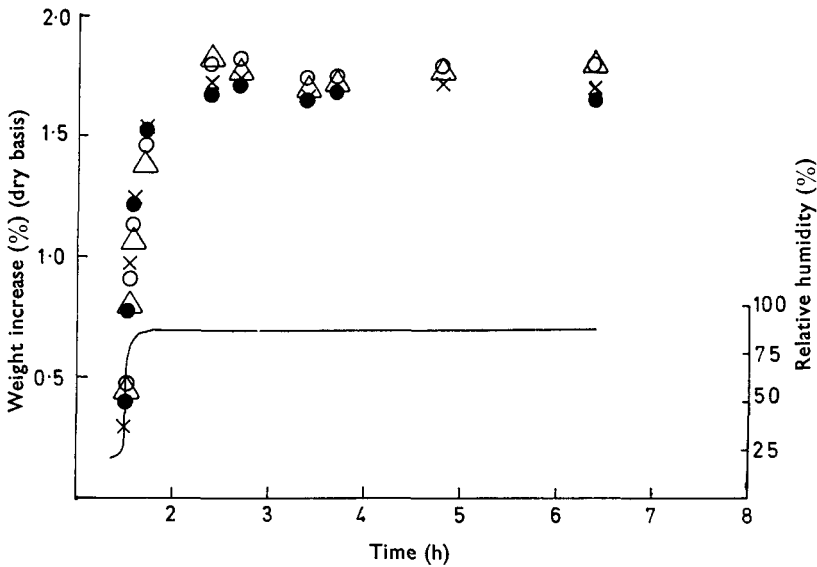


FIG. 7. The effect of bulk density on the moisture uptake of calcium phosphate at similar bed depths. Bulk densities (g ml^{-1}) ●, 0.160; ×, 0.184; ○, 0.218; △, 0.312. Bed depth (cm), ●, 1.15; ×, 1.20; ○, 1.15; △, 1.15.

bulk densities for this material (calcium phosphate) varied from the most open state of packing, produced on dredging, to a high density produced by tapping the material in the final container without a normal consolidating load. The tensile strengths of samples at various relative humidities and moisture contents are shown in Figs 8 and 9. The results are presented as tensile strength versus packing

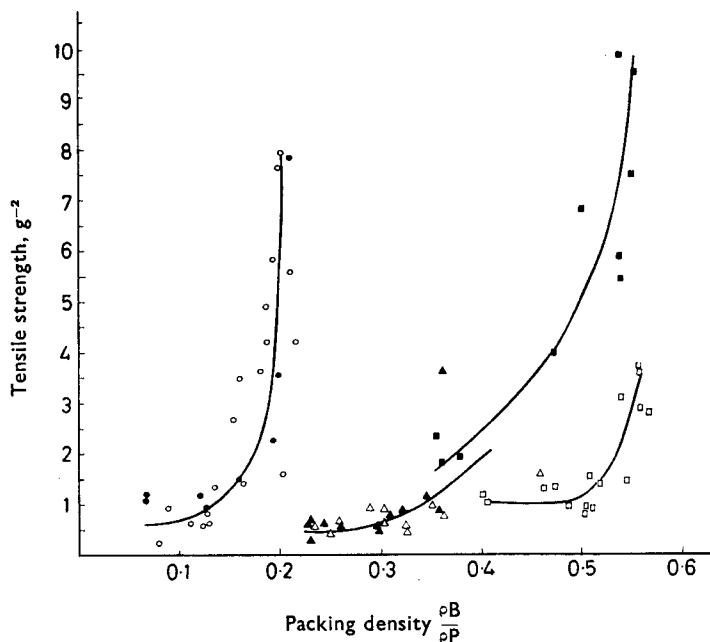


FIG. 8. Tensile strength of fine particle size materials. % w/w loss on drying calcium phosphate: ○, 1.01; ●, 1.8; lactose: △, 5.1; ▲, 5.27; potato starch: □, 17.7; ■, 23.2. RH (%) ○, △, □, 55; ●, ▲, ■, 86.

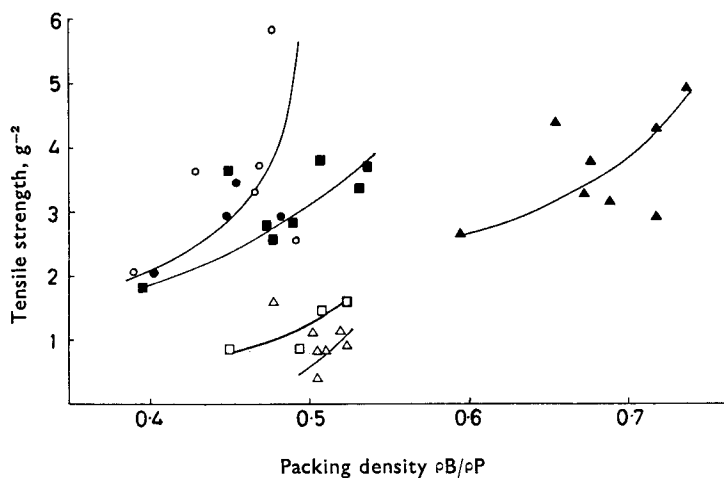


FIG. 9. Tensile strength of coarse particle size materials on exposure to high relative humidities. Potassium chloride; ○, 29 h; ●, 53 h at 88% RH. Sodium chloride: □, 4 h, ■, 52 h, at 76 → 80% RH. Sucrose △, 15 h; ▲, 98 h at 85% RH.

density, $\frac{\rho_B}{\rho_P}$ (Cheng, 1968), where ρ_B = bulk density g ml⁻¹, ρ_P = particle density g ml⁻¹.

From Fig. 8 it can be seen that for lactose and calcium phosphate, the small difference in moisture content at varying relative humidities does not produce a significant change in tensile strength. For potato starch, however, the higher equilibrium

moisture content at an elevated relative humidity causes an increase in tensile strength.

The results for sodium and potassium chloride and sucrose (Fig. 9) are more scattered but follow a similar pattern to those obtained for the other materials (Fig. 8). At low relative humidities, tensile strengths could not be measured on these materials due to their non-cohesive, free flowing nature. However, on exposure to high relative humidities, the values of tensile strength obtained were of equivalent magnitude to those for the more cohesive, fine particle size, bulk solids shown in Fig. 8.

DISCUSSION

It has been shown that free moisture exists in beds of bulk solids in at least two states; a 'pendular' state where liquid bridges occur between individual particles and a 'capillary' state where all the pores of the bed are filled with liquid which forms concave menisci at the pore ends. A 'transition' region between these two states is also suggested (Pietsch, 1967). For the thin beds of sodium chloride, potassium chloride and sucrose, the increase in moisture content, illustrated by Fig. 6, is accompanied by changes from the 'pendular' state through to the 'capillary' state. The significant changes in tensile strengths obtained for these materials, Fig. 9, may, therefore, be explained by the changes in the number and magnitude of the surface tension forces during the transition from various states of moisture location.

During moisture uptake the particle sizes of the sodium and potassium chloride and sucrose decrease by dissolution. The volume decrease of sodium chloride on the addition of 20% w/w water can be shown by calculation to be 7% (assuming that a saturated solution is formed). Thus, considering a median size of 214 μm , this would produce a median particle size of approximately 200 μm on dissolution. Since this size is still in the non-cohesive range the changes in tensile strength produced cannot be attributed solely to a reduction in size. The moisture must be evenly distributed throughout the material in the test cell for tensile strengths of beds determined in this manner to be meaningful. Table 5 shows the distribution of moisture at various depths in 1.1 and 6.2 cm-deep beds of sodium chloride. The results were obtained by exposing the upper surface only of the beds to a relative humidity of 90% for varying periods of time and determining the loss on drying of incremental sections. It can be seen that at low total moisture contents there is an uneven distribution of the water but as the moisture content increases reasonably uniform distributions occur, a higher moisture content being necessary in the thick beds for this state to be reached. This even distribution of moisture remains until the "capillary" state is reached when subsequent moisture uptake produces a supernatant layer.

Thus for those materials which do not exhibit a finite equilibrium moisture content, since their vapour pressures are below the partial pressure of the air-water mixture to which they are exposed, it is essential to use thin layers for humidification so that moisture distribution is uniform. For those materials that do reach an equilibrium moisture content at the relative humidities used, these bed depth considerations are less important, provided equilibrium is achieved. However, prolonged exposure times may be involved if the beds are excessively thick.

For potato starch the equilibrium moisture content obtained at 85% relative humidity agrees with the results obtained by Shotton & Harb (1965), but the tensile

Table 5. Variation in moisture content throughout beds of sodium chloride 1.1 cm and 6.2 cm in depth

Total % w/w loss on drying	Bed depths 1.1 cm		Total % w/w loss on drying	Bed depths 6.2 cm	
	% depth from exposed surface	% w/w loss on drying between stated depth		% depth from exposed surface	% w/w loss on drying between stated depth
0.68	0		0.56	0	
	25	1.07		5	4.1
	55	0.99		20	1.9
	100	0.27		41	0.16
					0.06
3.49	0		3.52	61	0.11
	18	3.9		100	
	47	3.5		0	5.9
	71	3.3		12	
	91	3.2		26	5.3
	100	3.5		46	5.1
				63	4.5
				77	1.2
8.75	0		5.30	100	0.5
	24	8.9		0	5.8
	49	8.3		10	5.4
	71	8.3		26	5.3
	94	8.9		42	5.2
	100	11.6		59	5.1
				77	5.1
					5.3
14.04	0		6.58	100	
	27	14.1		0	6.6
	50	13.5		13	6.1
	77	13.9		35	6.1
	96	14.6		49	6.3
	100	15.7		64	6.5
					6.5
20.72	0			79	7.6
	25	20.4		100	
	47	20.1			
	72	20.8			
	96	21.4			
	100	21.9			

strengths obtained by Shotton & Harb (1966) at similar equilibrium moisture contents are lower than the values obtained in this work.

This is probably due to the use of a different packing density (not specified by Shotton & Harb, 1966) since their method of bed preparation involves dredging with no consolidation.

This emphasizes the importance of packing density as a variable in tensile strength determinations. A small change in the contact distance or co-ordination number of the particles in a bed of bulk solid will produce a significant change in the nature of interparticulate bonding. The shape of the curves in Fig. 8 illustrates this point and is confirmed by the results of Farley & Valentin (1967-68) and Aoki & Tsunakawa (1969).

The moisture present in the samples of lactose and calcium phosphate at equilibrium with high relative humidities is likely to approach the pendular state only; the tensile strengths are not significantly different.

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