

Some observations on the ageing of sodium chloride compacts*

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The diametrical crushing strength of an ideal system of compacted particulate material, and the relation between strength and mean compaction pressure depend on the time at which the strength is determined. Strength increases of over 100% during the first hour after compression are attributed to stress relief of the sodium chloride crystals and interparticulate bonds. The effects of elevated temperature, and also humidity, on the strength and physical structure of compacts are evaluated. Relaxation behaviour of compacts containing light liquid paraffin is also investigated.

Changes in the mechanical properties of compressed tablets with time after compaction may influence their subsequent behaviour. Although such changes have been observed in industry nothing has been published about the significance of these effects.

The need to include a time factor has been recognized. Higuchi, Rao & others (1953) stated that the tablets were prepared and tested on the same day. Ganderton (1962) determined the crushing strength of compacts within 5 min of their ejection, whereas Lewis (1964) recorded the crushing strength of compacts "immediately" after their preparation. A delay of 6 h was standardized by Shotton, Deer & Ganderton (1963), and one month was quoted by Nelson, Arndt & Busse (1957).

We therefore examined the effects of several variables on the changes of strength with time of an ideal system of compacted material after its ejection from the die.

EXPERIMENTAL AND RESULTS

Sodium chloride (30-40 mesh) dried at 110° was used to form compacts without the addition of excipients. Weighed samples were compressed in a 1.2 cm (diameter) die between plane-faced punches in conjunction with an instrumented eccentric tablet press as described by Rees & Shotton (1969). In all compression experiments, each sample consisted of sufficient sodium chloride (982 mg) to produce a compact of 0.4 cm theoretical length at zero porosity.

Effect of time

Compacts were prepared in a "conditioned" die (Rees & Shotton, 1969) at a mean compaction pressure of 1200 kg cm⁻², and stored at 25° over silica gel. At selected time intervals the strength of a random sample of five compacts was determined by diametrical compression using the instrument described by Shotton & Ganderton (1960a). During the first hour, the strength increased by approximately 100% com-

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pared with the initial value (Fig. 1). Although the mean strength was further increased by approximately 1 kg after 140 h, Student's *t*-distribution showed only 60% probability that a significant change occurred subsequent to the first hour.

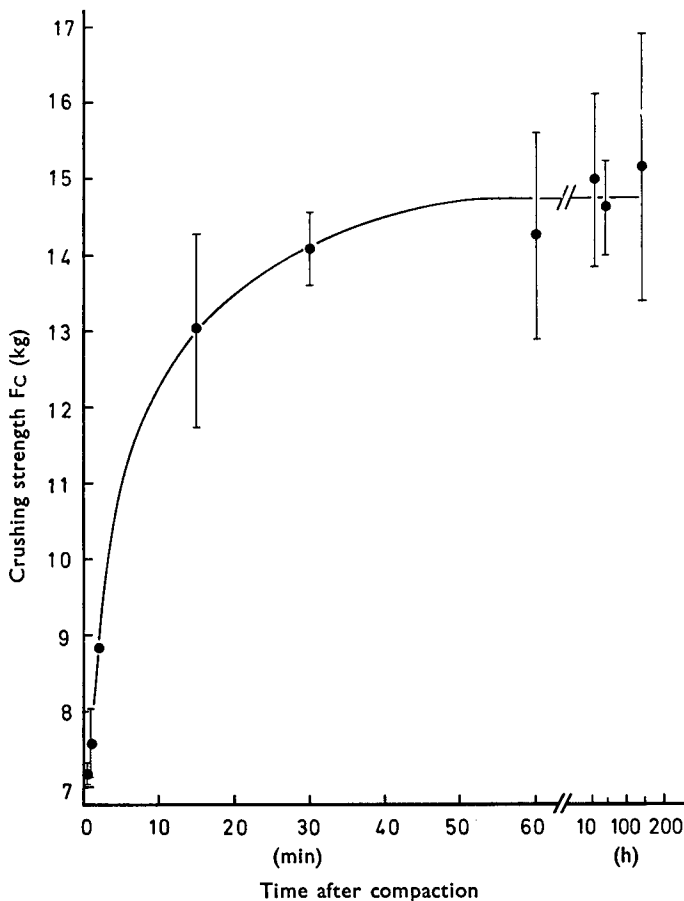


FIG. 1. Effect of time on the strength of sodium chloride compacts. Each co-ordinate represents the mean of five determinations and the standard deviation of each value is shown.

Effect of compaction pressure

The influence of compaction pressure on the changes in strength with time was evaluated, and the effects of storing compacts at 25° and at 100° were also investigated. Before preparing compacts at each pressure, the die was cleaned and conditioned.

The crushing strengths of five, randomly-selected compacts prepared at each pressure were determined less than 1 min after ejection. A linear relation was observed between the strength and mean compaction pressure, P_m , over the pressure range 0–2000 kg cm⁻² (Fig. 2). A second group of five replicate compacts was stored over silica gel at 25° for 1 h, and five compacts prepared at each pressure were stored in an oven at 100° for 1 h. Increases in strength of up to 115% were observed. The relation between the compaction pressure and the strength was linear to 1250 kg cm⁻² (123 MNm⁻²), but at higher pressures a decrease in slope occurred (Fig. 2).

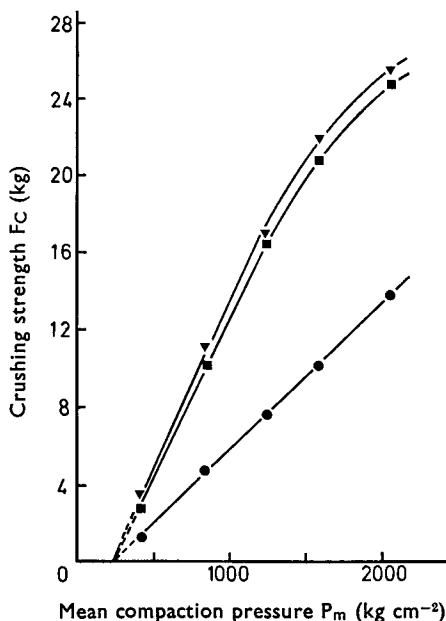


FIG. 2. Relations between the crushing strength and mean compaction pressure for compacts tested ●, immediately after ejection; ■, after 1 h at 25°; and ▼, after 1 h at 100°.

The increases in strength of compacts heated at 100° were only slightly greater than for those stored at 25°. Student's *t*-test analysis of the results for low compaction pressures indicated a significant difference between the mean strengths of compacts stored at the two temperatures. With increasing compaction pressure, there was a decrease in the statistical significance of the different values. However, in view of the apparent effect on certain compacts of heating at 100°, it was decided to dry compacts at 60° in other aspects of this investigation. Preliminary experiments had shown that this lower temperature did not affect the crushing strength of compacts prepared from dried material.

By extrapolation to zero crushing strength (Fig. 2), all three linear relations intercepted the pressure axis at 220 kg cm^{-2} , P_m (21.6 MNm^{-2}).

Effect of liquid films

The possible influence of interparticulate surface films was also studied. Owing to the problem of maintaining a constant moisture content by preventing evaporation or crystallization, experiments with compacts containing moisture were unsuccessful. For this reason, light liquid paraffin (B.P.C.) was selected as a non-volatile, non-solvent liquid and 2% by weight was added to a bulk quantity of the sodium chloride, and dispersed by standardized agitation. The weight of each sample for compression was calculated on the basis of sufficient *solid* to produce a compact of 0.4 cm length at zero porosity.

The effect of removing liquid films from the system after compaction was evaluated by solvent extraction of compacts using chloroform. Preliminary experiments with a series of compacts prepared from dried sodium chloride at a range of pressures demonstrated that this technique produced no significant changes in the weight, or crushing strength.

No direct assessment was made of the uniformity of distribution of the light liquid paraffin but the uniformity in weight of the compacts after removal of the liquid indicated that the replicate samples of compressed material were identical.

Table 1 shows the effect of time, and the influence of solvent extraction, on the crushing strength of compacts compressed with 2.0% light liquid paraffin.

Immediately after compression, the strength of compacts containing the paraffin (Table 1) was slightly less than the value of 7.6 kg, shown in Fig. 2, for compacts of dry material compressed in a conditioned die at $1220 \text{ kg cm}^{-2} P_m$. Compacts which were extracted with chloroform immediately after compression exhibited a final strength comparable to the value of 16.0 kg for compacts of dry material. However, the final strength of compacts containing the paraffin was approximately 3 kg below this value.

Table 1. *The effect of time of storage, and the influence of solvent extraction, on the strength of sodium chloride compacts compressed with 2.0% light liquid paraffin. Mean compaction pressure = 1220 kg cm^{-2} (120 MN_m^{-2}).*

Solvent extraction commenced at time:	Strength of compacts measured at time:	Crushing strength (kg) as mean of five replicates	Standard deviation, % of mean strength
—	<1 min	6.47	± 6.8
<1 min	8 h	16.57	± 18.4
—	8 h	13.16	± 12.8

Effect of humidity

The presence of moisture at the interparticulate junctions and at the die wall boundary has been shown to influence the compaction behaviour of sodium chloride and the crushing strength of the compacts produced (Shotton & Rees, 1966; Rees, 1970).

To distinguish any direct influence of moisture on the crushing strength, from the lubricant and hydrodynamic properties, compacts of dry material were exposed to 66 or 76% relative humidity for eight weeks. To minimize exchange of water vapour between the compacts and atmosphere during strength measurements, the ambient conditions were maintained in equilibrium with the samples, and the exposure time was as short as possible. Additional samples of the compacts exposed to humid conditions were dried at 60° for 1 h and cooled in a desiccator before their crushing strength was determined.

The effects of humidity on the mean strength, the strength variation and the moisture content are shown in Table 2. The moisture content of compacts was determined by a thermogravimetric technique using a Cahn Gram Electrobalance. Samples were dried at 110° and cooled in a vacuum on the balance as described previously (Shotton & Rees, 1966), to prevent errors arising from sample transfer.

Compacts stored at 76% relative humidity possessed a very low strength compared with the control samples. Subsequent drying of these compacts produced only a small increase in the mean strength, but a large standard deviation of strength values was observed. Conversely, for the compacts stored at 66% relative humidity, drying caused a large increase in strength, despite the small moisture sorption which had occurred on storage.

Table 2. *The crushing strength and moisture content of sodium chloride compacts stored at elevated humidity for eight weeks. Mean compaction pressure = 1273 kg cm⁻² (125 MNm⁻²).*

Storage conditions	Treatment	Crushing strength* (kg)	Standard deviation (% of mean)	Moisture content (%)
Desiccator	—	16.27	12.4	0.00
66% RH	—	17.30	2.1	0.005
66% RH	Dried	25.82	5.4	0.00
76% RH	—	1.91	7.9	0.50
76% RH	Dried	2.67	19.9	0.00

* Each value is a mean of 10 replicates.

DISCUSSION

Non-linear arithmetic relations between crushing strength and compaction pressure were reported by Higuchi & others for a sulphathiazole granulation (1953) and for aspirin and lactose (1954). Shotton & Ganderton (1960a) and Lewis (1964) also obtained non-linear relations for sodium chloride (30–40 mesh), a plot of crushing strength versus mean compaction pressure showing a continual decrease in slope. However, the present results indicate that the relation for sodium chloride is linear up to 2050 kg cm⁻²P_m, provided the crushing strength of the compacts is evaluated within 1 minute of ejection from the die.

Using the Cahn Gram Electrobalance, we found no moisture in the samples for compression. Consequently, increases in strength of the magnitude observed after ejection cannot be explained in terms of interparticulate deposition of crystallized material from surface moisture films (cf. Shotton & Rees, 1966).

Baba & Nagafuji (1965) have shown for several materials, including sodium chloride, that there is a measurable strain recovery of compacts during the period immediately after compression. For compacts of sodium chloride, compressed to 15 mm length at 2230 kg cm⁻² pressure using 20 mm diameter plane-faced punches, these authors found that 0.2% axial strain recovery occurred in the die after removing the applied pressure. After ejection, there was further strain recovery of 0.9% in the axial direction and 0.2% in the radial direction. We believe that the strength increases we observed are due to this time-dependent relaxation which provides stress relief within the compact. Increased bonding may occur if elastic or plastic flow increases the area of intimate contact between adjacent crystals. The deviation from a linear relation (Fig. 2) for compacts stored for 1 h may then be attributed to incomplete strain relief which occurs when the structure of the compact permits only partial relaxation of crystals. As the porosity of a compact is reduced, the strength will approach a maximum value corresponding to the intrinsic strength of the solid material. However, for compacts tested immediately after compression, there is no evidence of a limiting value of crushing strength at a mean compaction pressure of 2050 kg cm⁻² (201 MNm⁻²).

Although an elevated temperature may encourage further strain relief due to an increase in the plasticity of the crystalline material (Sperling, 1932), it is also possible that small increases in crushing strength of compacts stored at 100° are produced by an increase in surface energy. Crone & McKee (1950) stated that an increase in temperature removes adsorbed films so that surface forces are able to act to the fullest extent, although the absolute magnitude of the forces is probably decreased.

For compacts of sodium chloride it has been shown that the shear strength and crushing strength are similarly related to a parameter such as the porosity (Ganderton, 1962). It is interesting therefore, that Lewis (1964) observed a *decrease* in the shear strength of sucrose compacts with time, in contrast to the present results for crushing strength of sodium chloride.

Strain relief within a compact during ejection from the die may cause a reduction in strength and result in capping and lamination (Train, 1956; Long, 1960). The presence of lubricant confined to the die wall was shown by Shotton & Ganderton (1961) to have no effect on the strength or capping characteristics of hexamine, whereas coating the particles with a lubricant material before pressing weakened the interparticulate bond and prevented capping. Consequently, it is reasonable to assume that the effect of strain relief on the strength of a compact will depend on the rheological properties of the particulate solid material and of the interparticulate bonds that are produced by compression. For compacts containing 2% of light liquid paraffin, the strength after recovery was less than for compacts of dry material. This suggests that the liquid film does not facilitate recovery, for example by a lubricant effect or by modifying the physical properties of the crystalline material. Shotton & Rees (1966) concluded that a liquid of low viscosity could act as an interparticulate lubricant during compaction. The present results therefore suggest that, during recovery, no significant movement of the interparticulate boundary is involved and that strain recovery after ejection is predominantly an intrinsic property of the crystalline material and of interparticulate bonds. However, additional increases in strength occurred when the compacts were extracted during recovery. This result indicates that the removal of liquid films permits increased bonding, when areas of contact within a compact are increased by subsequent plastic or elastic recovery of the material.

The large decrease in standard deviation of replicate values of crushing strength on storage at 66% relative humidity (Table 2) is in agreement with the observation of Smothers, Kreglo & Moscker (1964) who tested the modulus of rupture of refractory brick, before and after immersion in water. They attributed the effects of water to a decrease in surface energy which reduces the strength distribution of flaws.

A reduction in surface energy will also reduce the overall strength of a compact. Since it is not certain that atmospheric conditions in the humidity chamber were uniform at all times, periodic dissolution and crystallization may have occurred. The slight increase in strength of compacts stored at 66% relative humidity may therefore have been caused by dissolution and removal of surface cracks and flaws in the crystals; these are known to act as centres of stress concentration.

Despite the large increases in the crushing strength on drying, of compacts stored at 66% relative humidity, the percentage standard deviation of replicate values was less than for the control samples. This is attributed to interparticulate crystallization of saturated solution within the compact causing a reduction in the incidence of crack propagation. The results suggest that small quantities of residual solvent may produce marked changes in the physical properties of a compact during storage.

No difference in microscopical appearance could be detected between the fractured surfaces of the control samples and the wet compacts stored at 66% relative humidity. However, the dried compacts exhibited a more planar fracture due to cross-grain failure (Shotton & Ganderton, 1960b, 1961) in the presence of strong bonds produced by interparticulate crystallization.

Examination of the compacts stored at 76% relative humidity showed that the original crystals (approximately 500 μm) had been almost entirely replaced by smaller crystals, and owing to the low strength of the interparticulate bonds, it was possible to detach a sufficient number of the crystals to estimate their mean size, which was approximately 70 μm . Deliquescence of sodium chloride occurs when the relative humidity exceeds 76%. The observed structure may therefore be attributed to extensive dissolution and subsequent recrystallization which could occur repeatedly following small fluctuations in the storage conditions. Consequently, the compact may no longer represent the original compacted system, since to a large extent, the interparticulate bonds formed during compaction will be removed by dissolution. New bonds will then form by recrystallization of dissolved solid material within the compact. The increased number of discontinuities which can propagate failure of the compact will contribute appreciably to the pronounced decrease in strength.

The large standard deviation in the strength of compacts which were dried after storage at 76% relative humidity, may be explained by a large variation in the strength of the bonds formed by further crystallization between the small crystals.

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