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THE EFFECT OF THE SPECIFIC SURFACE AREA OF HEAVY MAGNESIUM CARBONATE ON ITS TABLETING PROPERTIES

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ABSTRACT

Heavy magnesium carbonates, either granules or spray dried powders were prepared at five different temperatures respectively. It has been found that the specific surface area of the magnesium carbonates prepared at lower temperatures is higher than that prepared at higher temperatures. The moisture adsorption (%) of magnesium carbonates and the crushing strength of the magnesium carbonate compacts prepared at five pressure ranges showed linear relationships with the specific surface area of the magnesium carbonates. However, Heckel plots indicated that magnesium carbonates prepared at higher temperatures were more compressible.

INTRODUCTION

Interbatch variation in the physical properties of heavy magnesium carbonate powder was noticed previously[1]. However, causes of the variation were not clear. The manufacturing methods described in B.P.[2] and in Remington's Pharmaceutical Sciences[3] for the production of heavy magnesium carbonate are similar, but not quite the same. In B.P.[2], boiling and concentrated solutions are used for the manufacture of heavy magnesium carbonate; while in Remington's Pharmaceutical

Sciences[3], the reacting solutions are hot and concentrated only. It is thought that the difference in temperatures of the reacting solutions may have an effect on the physical properties of the heavy magnesium carbonate produced, which in turn, may affect its tableting properties.

MATERIALS

Magnesium sulphate, sodium chloride and acetone, (Union Chemical works Ltd., Taiwan, R.O.C.); Sodium carbonate and magnesium stearate, (Osaka Hayashi Pure Chemical Industries, Ltd., Japan); Toluene, (Riedelde Haen, West Germany); Isoton II^{R} (1% w/v saline), (Coulter Electronics Ltd., U.K.)

METHODS

Preparation of heavy magnesium carbonates

Heavy magnesium carbonate was prepared by addition of a hot and concentrated magnesium sulphate solution to a hot and concentrated sodium carbonate solution. For each preparation, the temperature of these two reacting solutions was kept at the same level. Five different temperatures, 60, 70, 80, 90 and 97°C were used. On the addition of these two reacting solutions together, heavy magnesium carbonate precipitated. The precipitate was washed and filtered three times and the wet magnesium carbonate was redispersed in distilled water. The suspension which was prepared at each temperature was then divided into two equal portions. Spray dried powder was obtained by spray drying of one of them. The other portion was filtered and the wet mass was evenly spread on a gypsumboard which was covered with a piece of cloth. The excess water in the magnesium carbonate mass was absorbed by the board. Subsequently, the magnesium carbonate mass was forced through a 500 um sieve and dried at 60°C for 24 hrs. The dry granules were sieved, and the fraction (250-500 um) was collected.

Before use, both of the granules and spray dried powders were dried in a vacuum oven at 60°C for 24 hrs, then kept in a desiccator.

Determination of the physical properties of heavy magnesium carbonates

(i) The true density of the solids was determined by a liquid displacement methods, which toluene (specific gravity 0.86 g/ml at 20°C) was the supernatant liquid.

(ii) The tapped bulk density of magnesium carbonates was determined using the Engelsmann bulk density apparatus (Stampfvolumeter, Stav 2003. J. Engelsmann AG., West Germany). The volume readings were taken at an interval of 50 taps until 500 taps were reached. Then the relative density (tapped bulk density/true density of powder) was calculated.

(iii) The angle of repose of the magnesium carbonates was determined by a fixed height (3.0 cm) method[4]. The mean results of six determinations for each powder are presented in Tables 1 and 2.

(iv) The median particle diameter (um) of the solids was determined using the Coulter Counter TA II/PCA/Accucomp™ system. Before size analysis, a standard pretreatment method[5] was applied for dispersion of the magnesium carbonates. The data given are the mean of 3 determinations.

(v) The specific surface area of the solids was determined on a Micromeritics Surface Area Analyser, 2200 by B.E.T. method. Prior to analysis, the magnesium carbonates were degassed in a vacuum oven at 70°C for 12 hrs. The data shown are the mean of 3 determinations.

(vi) For testing of moisture adsorption of the solids, the moisture content of the samples was determined after they were exposed to environment of known relative humidity (saturated sodium chloride solution, 75% R.H.[5]) for two months.

(vii) Electron micrographs of the solids were made using a scanning electron microscope (JEOL JSM-35CF SEM, Japan). Prior to examination, the solids were coated with gold using a sputtering device.

(viii) Compacts for crushing strength determinations were prepared using a hand operated hydraulic press. A weighed quantity of 380 mg was compressed at 5 pressure ranges, 50, 99, 148, 198, and 248 MNm^{-2} in a lubricated 12.5 mm internal diameter die respectively. The die and punches were lubricated with a 2% w/v of magnesium stearate in acetone prior to each compaction. After storage in a desiccator for 24 hrs, the crushing strength of the compacts was determined using a hardness tester (Model CT40, Enginerring Systems (Nottm.), U.K.). Prior to testing, the compacts were weighed and the thickness measured. The results quoted are the mean of 6 determinations.

RESULTS AND DISCUSSION

The physical properties of both spray dried and granulated heavy magnesium carbonates are summarised in Tables 1 and 2 respectively. As expected, due to the uniformity of granules, the granular form of magnesium carbonates has a comparatively lower value of angle of repose. The granular form of magnesium carbonates also gave a relatively higher value of bulk density than that of spray dry powders, except for the magnesium carbonate which was prepared at 97°C. The magnesium carbonates which were prepared at 80°C gave the lowest value of bulk density. The true density of the magnesium carbonates ranges from 2.10 to 2.39 g/ml. In the present study, a value of 2.23 g/ml[1] was adopted for the calculation of the relative density of magnesium carbonates.

Figures 1 and 2 show the plots of relative density vs number of taps for spray dried and granulated magnesium carbonates respectively. At any given number of taps, the magnesium carbonates which were prepared at 97°C gave the highest value of relative density. Whereas, the magnesium carbonates which were prepared at 80°C

Table 1. The physical properties of heavy magnesium carbonate powders.

Magnesium carbonate spray dried powder prepared at (°C)	60	70	80	90	97
Angle of repose θ^o	57	60	58	60	56
Bulk density (g/ml)	0.296	0.273	0.186	0.257	0.514
True density (g/ml)	2.21	2.23	2.10	2.17	2.39
Moisture adsorption (%)	5.16	3.82	3.66	2.39	1.46
Median particle diameter (µm)	14.7	14.7	9.4	9.0	13.4
Specific surface area (m^2/g)	15.53	13.62	14.01	7.84	4.41
Roughness $= \frac{\text{measured surface area}}{\text{calculated surface area}}$	84.8	74.4	48.9	26.2	21.9

gave the lowest value of relative density. The curves for the magnesium carbonates which were prepared at 60, 70 and 90°C were intermediate between them.

The curves for granulated magnesium carbonates reach a plateau after about 150 taps. Whereas, for spray dried magnesium carbonates the curves do not reach a plateau up to 500 taps, except for magnesium carbonate which was prepared at 97°C, the relative density reaches a plateau at 350 taps. The regularity in particle shape and better flowability of the granular form of magnesium carbonates may be attributed to the reaching of a plateau at an earlier stage of tapping of the solids. Comparatively, it will be more easier for them to achieve a steady packing.

Table 2. The physical properties of heavy magnesium carbonate granules.

Magnesium carbonate granulation prepared at (^oC)	60	70	80	90	97
Angle of repose θ^o	47	44	50	42	44
Bulk density (g/ml)	0.355	0.315	0.229	0.338	0.421
True density (g/ml)	2.10	2.15	2.10	2.28	2.32
Moisture adsorption (%)	4.84	3.76	3.73	2.14	1.48
Median particle diameter (μm)	14.1	16.3	10.9	10.4	15.2
Specific surface area (m^2/g)	18.21	16.70	16.40	10.40	7.80
Roughness $= \frac{\text{measured surface area}}{\text{calculated surface area}}$	95.4	101.1	66.4	42.1	44.1

A detailed examination of the samples using the Scanning electron microscope was carried out and a series of photomicrographs (Photographs 1-8) were taken to show the shape and surface characters of the particles. Essentially the particles are roughly spherical and are build up of plate-like structures. The particles of the magnesium carbonate which was prepared at 97^{o}C were build up of closely packed plate-like structures (Photographs 7-8). In comparison, the build up of plate-like structures for the particles of magnesium carbonates which were prepared at 60, 70, 80 and 90^{o}C respectively are less closely packed (Photographs 1-5). This may explain that magnesium carbonate which is prepared at 97^{o}C has the highest values of bulk density and tap density (at the highest number of tapping studied).

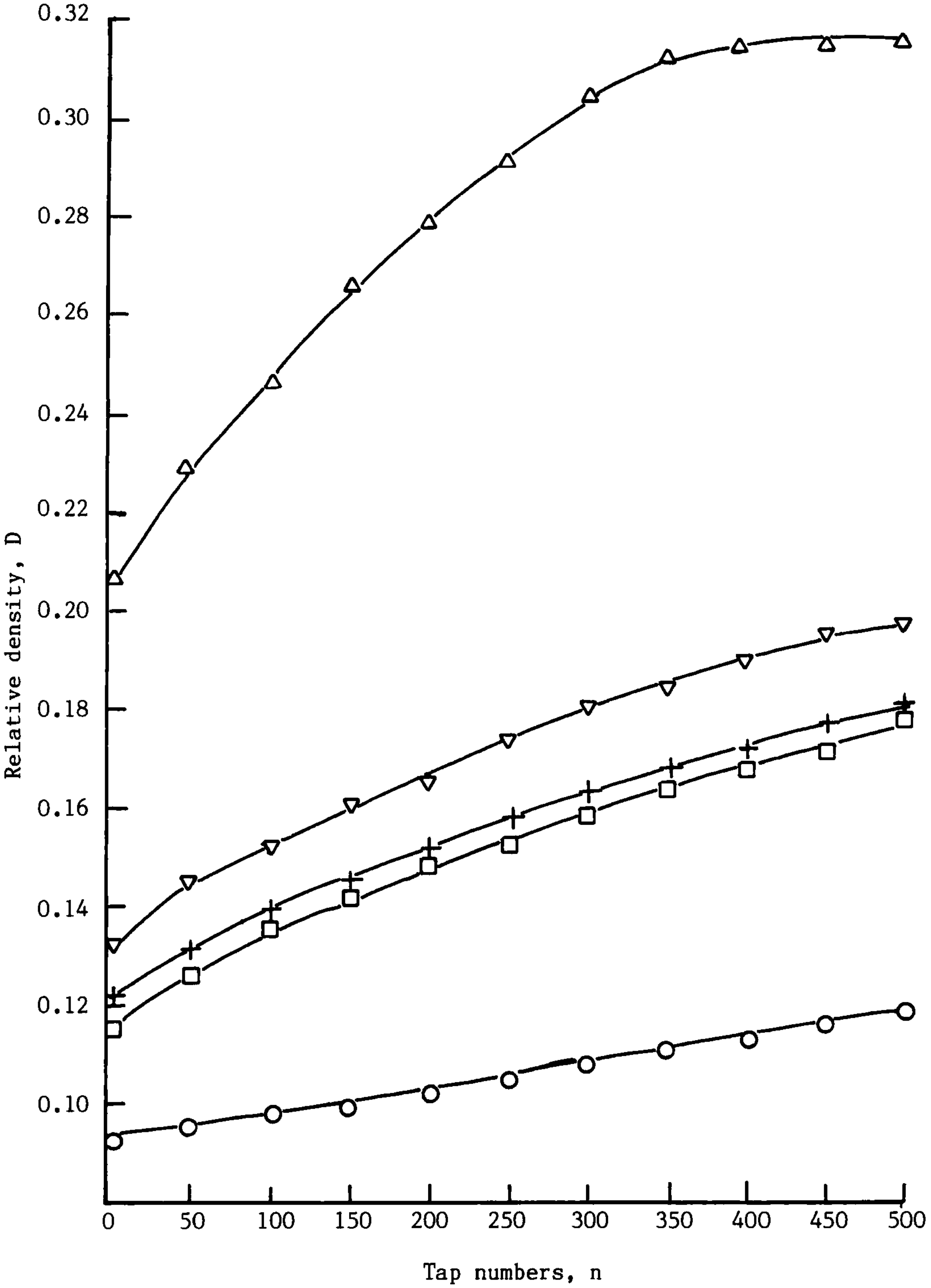


FIGURE 1

Relative density, D, vs tap numbers, n, for magnesium carbonates (powders) prepared at different temperatures. ▽ , 60°C; +, 70°C; ○ , 80°C; □ , 90°C; △ , 97°C

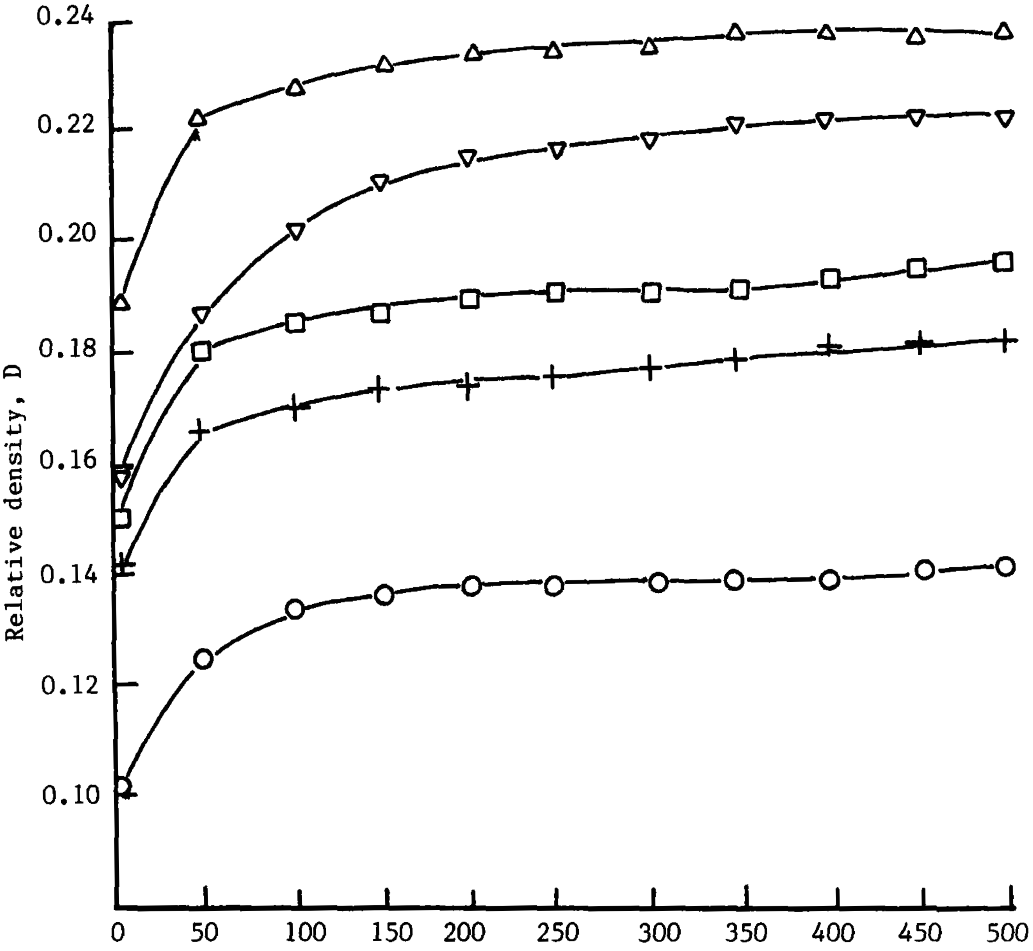


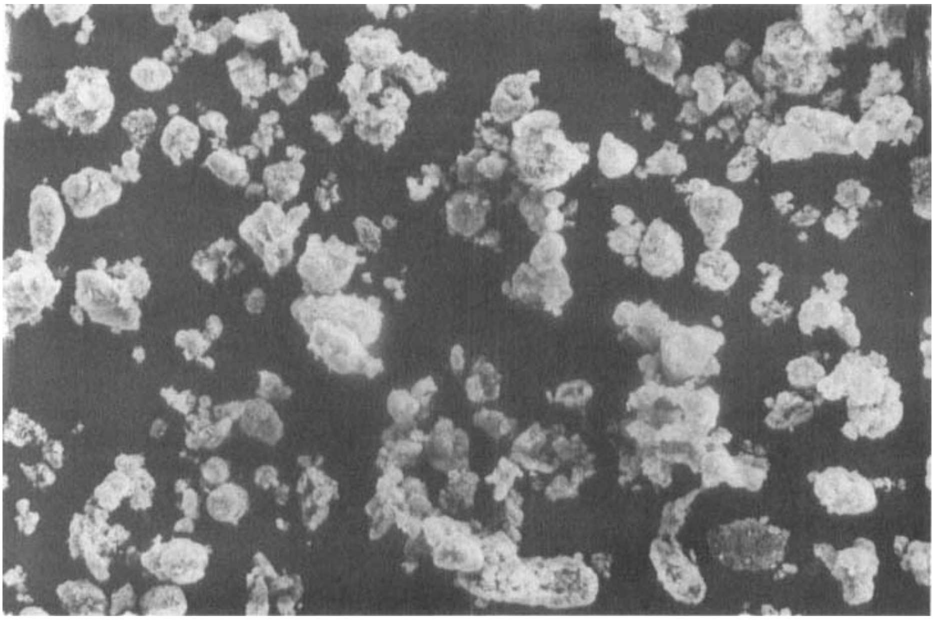
FIGURE 2

Relative density, D, vs tap numbers, n, for magnesium carbonates (granules) prepared at different temperatures. (Symbols as in Figure 1)

Figures 3 and 4 represent the relationship between compression pressure and the parameter ln(1/1-D)[7,8], where D is the relative density of the compact at pressure, P, for two forms of magnesium carbonates. In their use of the Heckel plot to study the consolidation of magnesium carbonate, Armstrong and Morton[9] attributed

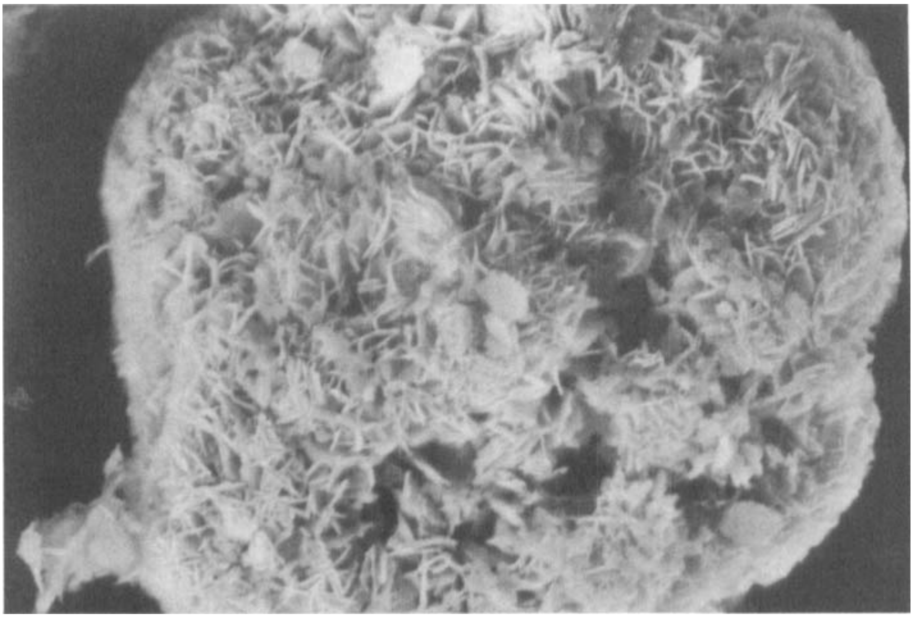
PHOTOGRAPH 1

Photomicrograph of magnesium carbonate prepared at 60°C. 19,000X



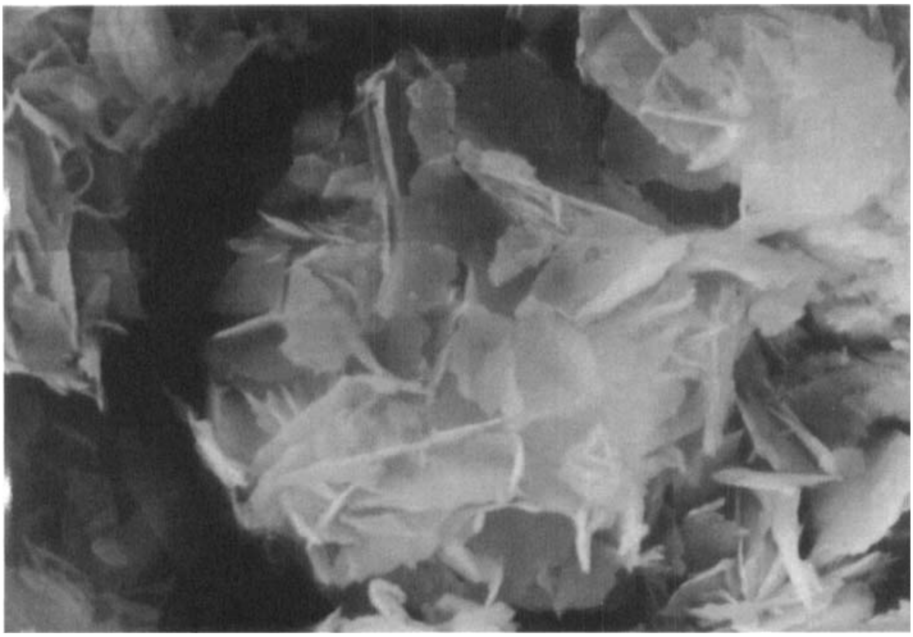
PHOTOGRAPH 2

Photomicrograph of magnesium carbonate prepared at 70°C. 570X



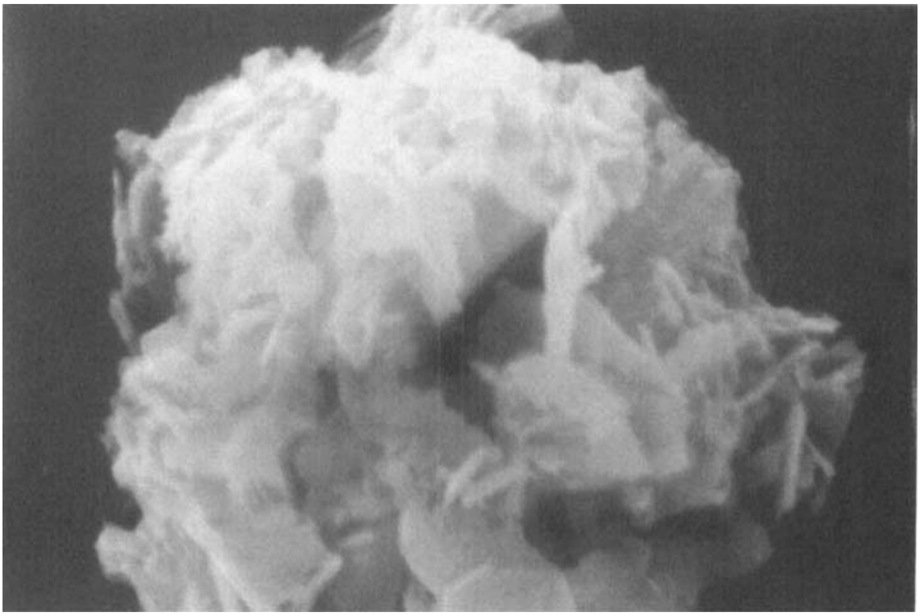
PHOTOGRAPH 3

Photomicrograph of magnesium carbonate prepared at 70°C. 5,700X



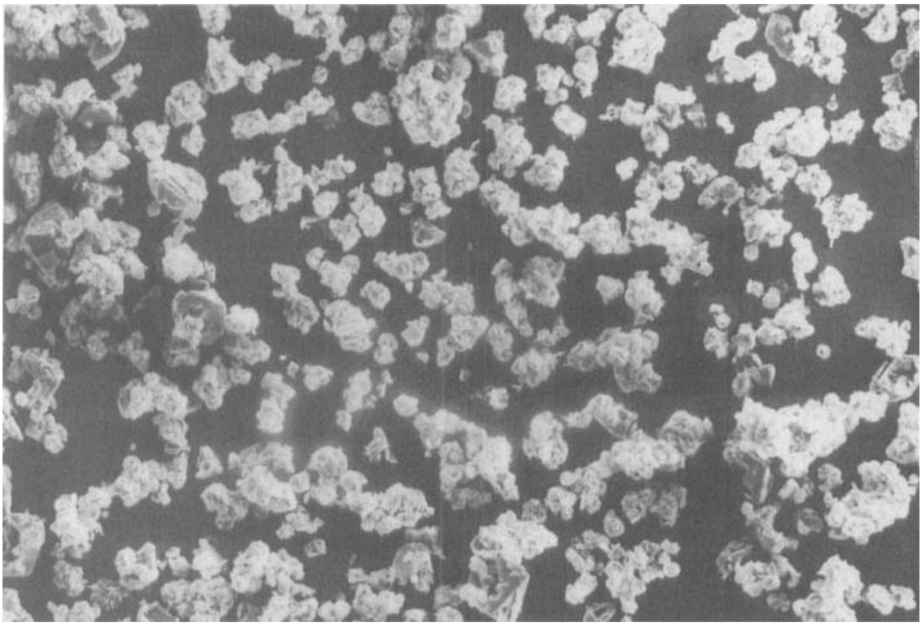
PHOTOGRAPH 4

Photomicrograph of magnesium carbonate prepared at 80°C. 9,500X



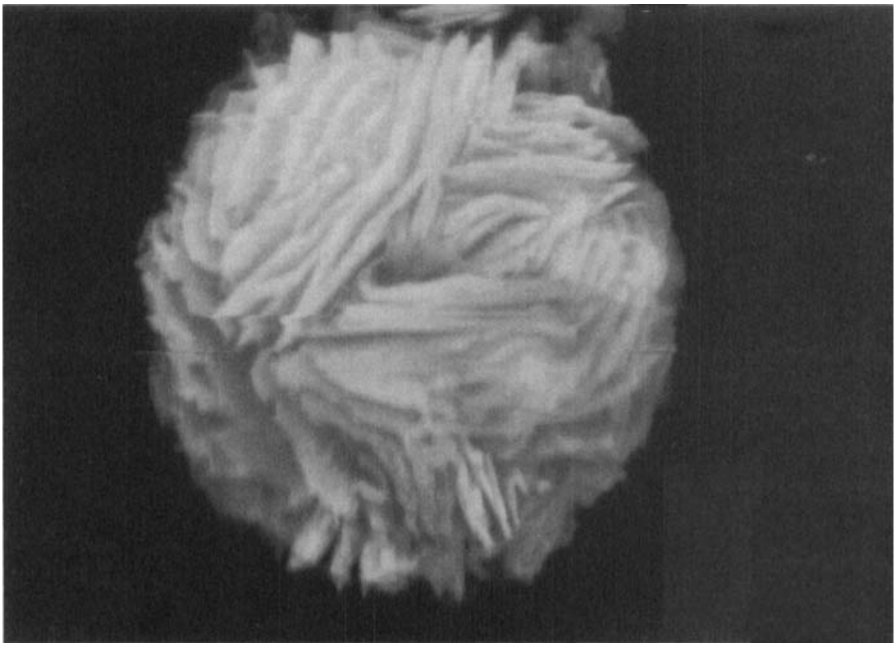
PHOTOGRAPH 5

Photomicrograph of magnesium carbonate prepared at 90°C. 19,000X



PHOTOGRAPH 6

Photomicrograph of magnesium carbonate prepared at 97°C. 570X

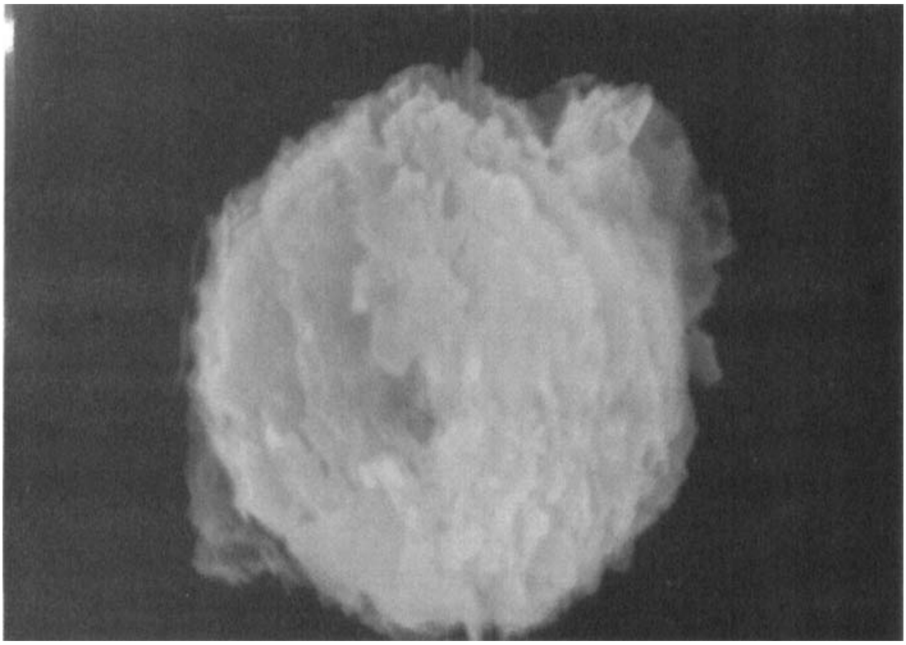


PHOTOGRAPH 7

Photomicrograph of magnesium carbonate prepared at 97°C. 19,000X

the good approximation to linearity of the plot to plastic deformation and interparticulate bonding taking place at the same time as particle fragmentation. In the present study, the Heckel plots for magnesium carbonates show a good approximation to linearity up to 248MNm^{-2} after an initial curved reponse.

Table 3 shows the results of linear regression analyses carried out from the curves in Figures 3 and 4 together with the derived parameters K, A, and P_Y. For which K and A are the values of slope and intercept of the curves respectively. P_Y is the yield pressure[10] of



PHOTOGRAPH 8

Photomicrograph of magnesium carbonate prepared at 97°C. 19,000X

the substances. The correlation coefficients show a highly significant relationship between P and ln(1/1-D). Table 3 also shows that there is an increase in the values of A and K, and a decrease in the value of P_Y for an increase in the preparation temperature of the magnesium carbonates. However, the magnesium carbonate which is prepared at a lower temperature will have a higher value of specific surface area (Tables 1 and 2). Therefore, it can be said that an increase in the value of specific surface area will increase the yield pressure of the magnesium carbonates.

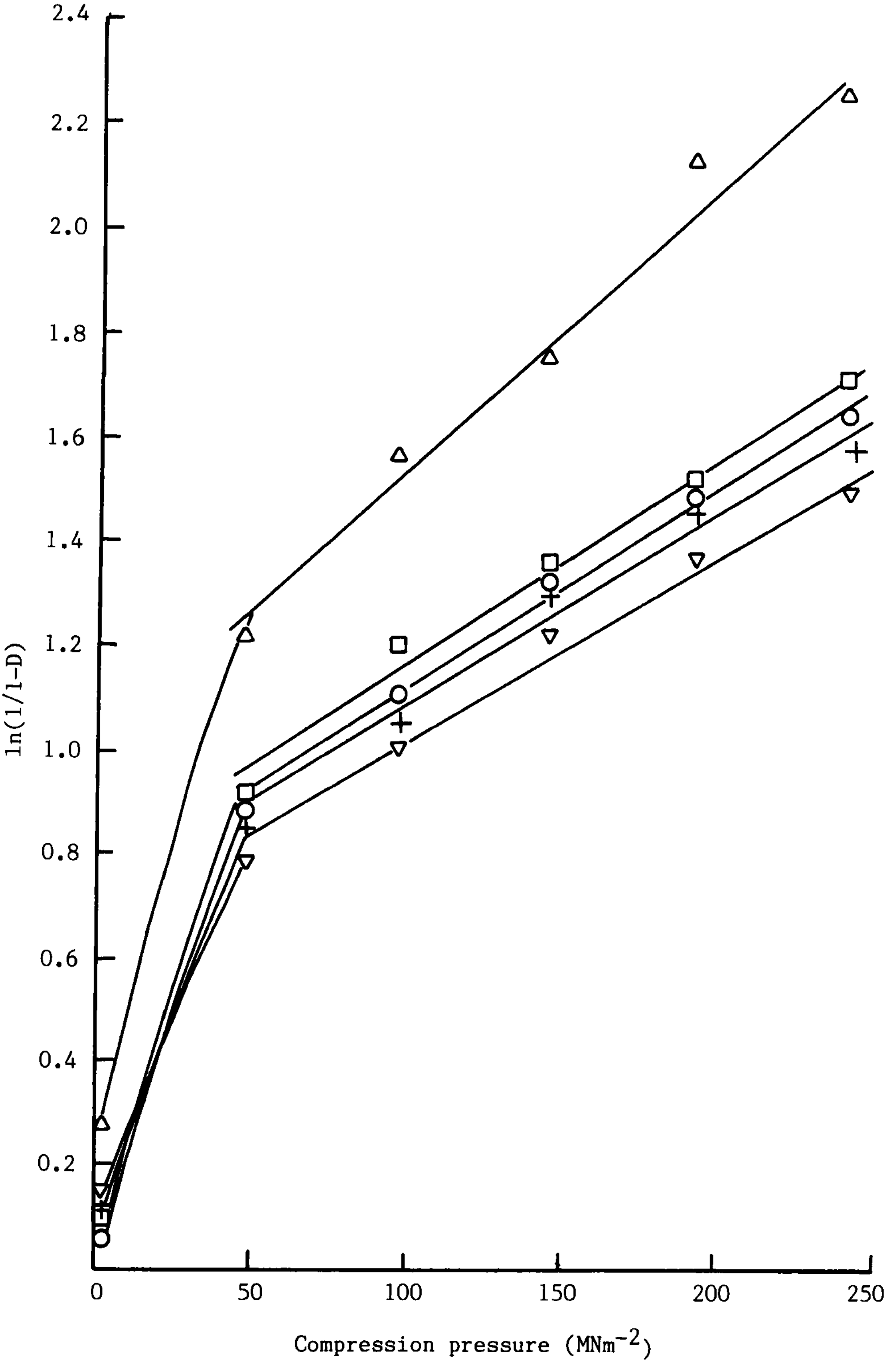


FIGURE 3

Graphs of ln(1/1-D) vs P for magnesium carbonates (powders) prepared at different temperatures. (Symbols as in Figure 1)

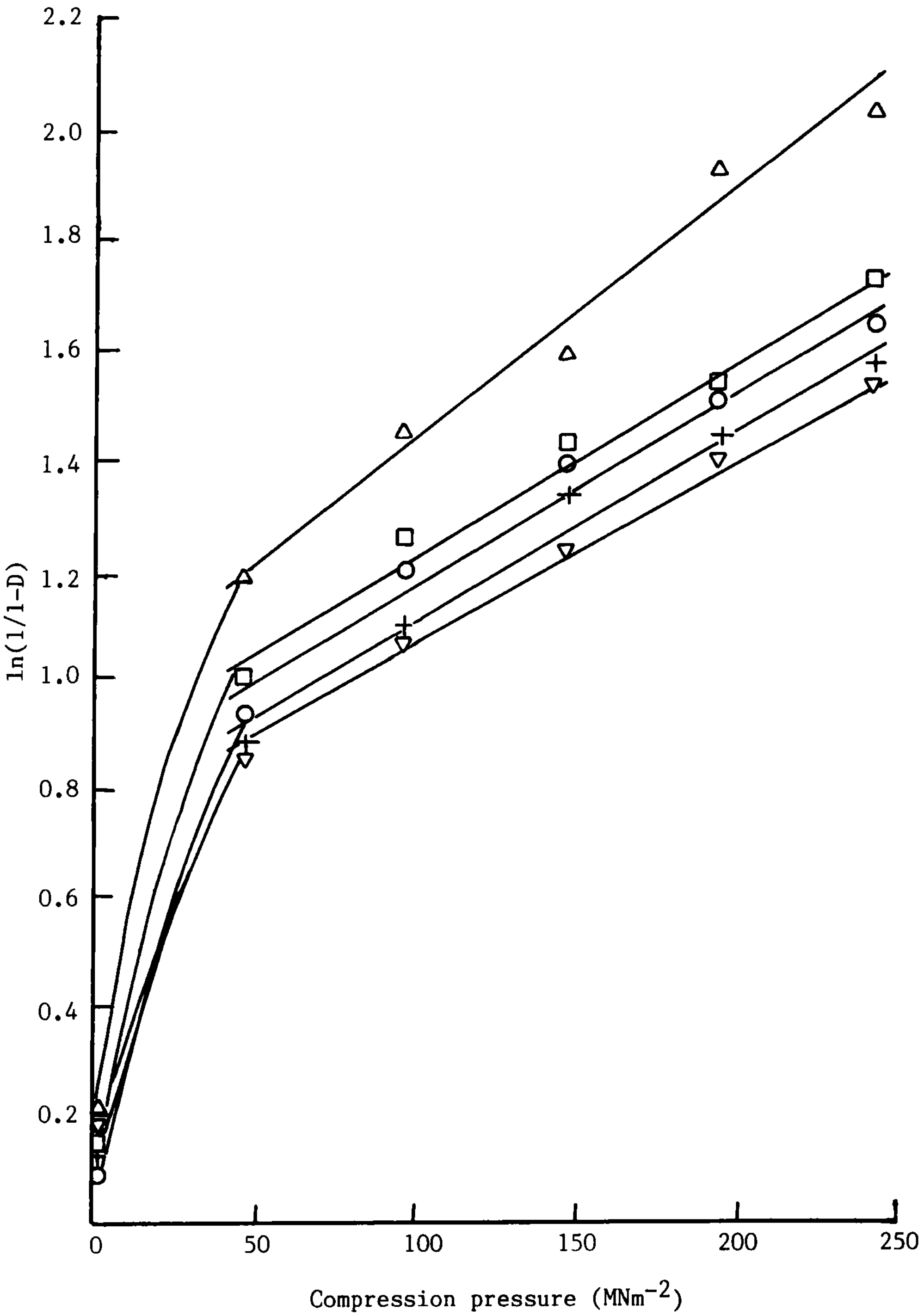


Figure 4

Graphs of ln(1/1-D) vs P for magnesium carbonates (granules) prepared at different temperatures. (Symbols as in Figure 1)

Table 3. The results of linear regression analyses carried out from Figs. 3-4.

Magnesium carbonate		Preparation Temperature (^{o}C)				
		60	70	80	90	97
Granules	Correlation Coefficient $\times 10^{-3}$	989	988	986	992	989
	Intercept A $\times 10^{-3}$	732	751	812	861	975
	Slope K $\times 10^{-5}$ (m^2MN^{-1})	335	354	361	359	450
	Yield Pressure P_Y (MNm^{-2})	298	282	277	278	222
Spray dried powders	Correlation Coefficient $\times 10^{-3}$	986	982	990	993	992
	Intercept A $\times 10^{-3}$	660	719	729	772	1004
	Slope K $\times 10^{-5}$ (m^2MN^{-1})	353	368	384	387	527
	Yield Pressure P_Y (MNm^{-2})	283	272	260	258	190

Table 4. Values of D_o, D_A and D_B for magnesium carbonates prepared at various temperatures (°C).

Magnesium carbonate		Parameter		
		D_o	D_A	D_B
Granules	60	0.159	0.519	0.360
	70	0.141	0.528	0.387
	80	0.103	0.556	0.453
	90	0.152	0.577	0.425
	97	0.189	0.623	0.434
Spray dried powders	60	0.133	0.483	0.350
	70	0.122	0.512	0.390
	80	0.083	0.518	0.435
	90	0.115	0.538	0.423
	97	0.230	0.593	0.363

Table 4 shows the experimental values of D_o and the calculated values of D_A and D_B. D_A and D_B were calculated using Equations 1 and 2[8] respectively.

$$D_A=1-e^{-A} \quad \text{------------------(1)}$$

$$D_A=D_o+D_B \quad \text{------------------(2)}$$

Two forms of magnesium carbonates which were prepared at 80°C gave the lowest value of D_o and highest value of D_B. The comparatively high value of D_B for these two magnesium carbonates showed that there was a greater degree of particle rearrangement and movement taking place during the early compression of these substances. However, Armstrong and Haines-Nutt[11] has shown that considerable fragmentation of magnesium carbonate takes place at pressure below $60MNm^{-2}$ and so it is reasonable to assume that rearrangement and fragmentation are both taking place at this point ($50MNm^{-2}$). At any given number of taps the values of relative density for these two magnesium carbonates are the lowest among the samples studied, indicating that these two samples are not capable of packing into a relatively denser packing due to particle rearrangement (Figures 1 and 2). While photomicrographs show that the particles of these two samples are build up of loosely packed plate-like structures (Photograph 4), which will be expected to fragment more easily at a relatively low pressure and give a higher value of D_B.

The relative density of the magnesium carbonates obtained at the highest number of taps is neither quantitatively nor qualitatively comparable to the D_A value of the solids obtained by extrapolation of the Heckel plots of the solids to zero compression pressure. This is expected as the particles have fragmented in the early stage of compression and no particle fragmentation is expected on tapping.

Figure 5 shows that the value of moisture adsorption (%) is higher for the magnesium carbonate having a higher value of specific surface area. The surface area which is available for moisture adsorption will be greater for magnesium carbonate having a higher value of specific surface area.

Smaller particle size is expected to produce stronger tablets due to comparatively greater interparticulate contact area. Shotton and Ganderton[12] found that for sodium chloride (120-400 um) and hexamine (150-500 um) compacted at a constant compression pressure, a logarithmic decrease in crushing strength with the increased particle size.

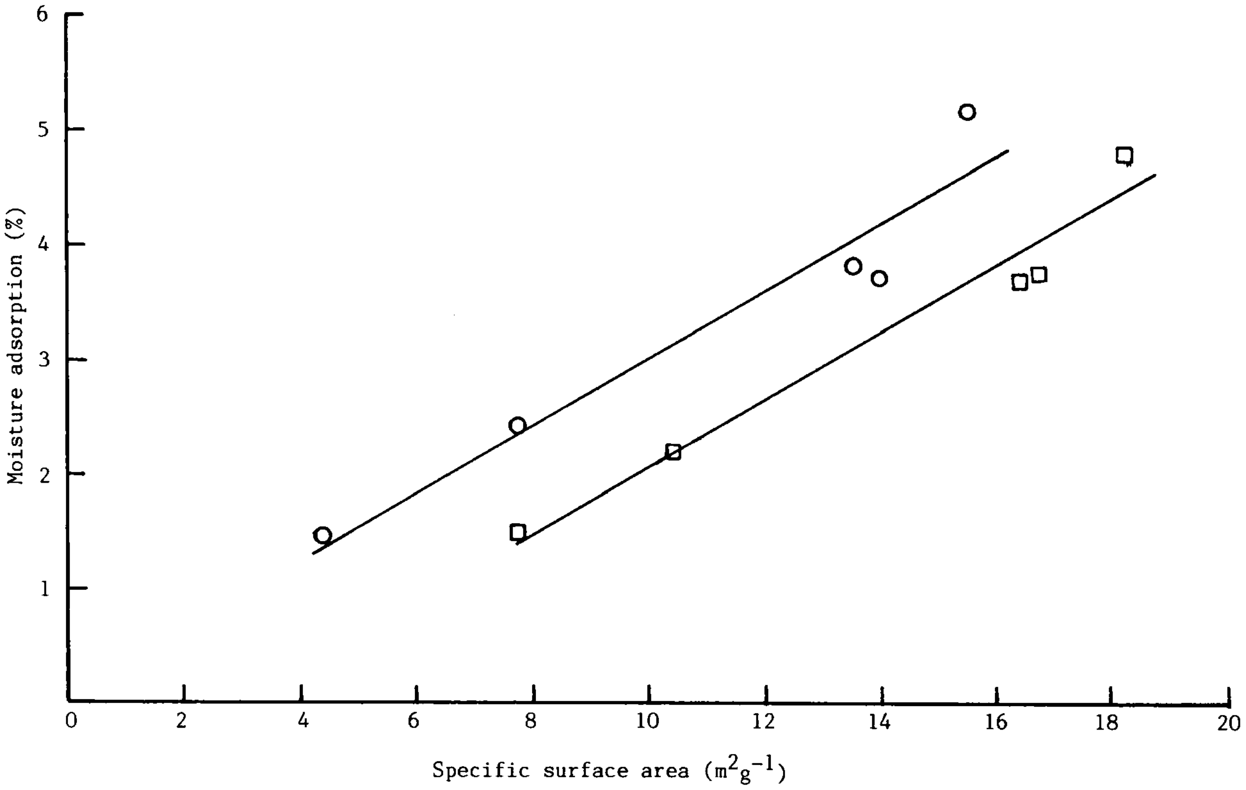


FIGURE 5

Moisture adsorption (%) vs specific surface area for magnesium carbonates. ○ , Powders; □ , Granules

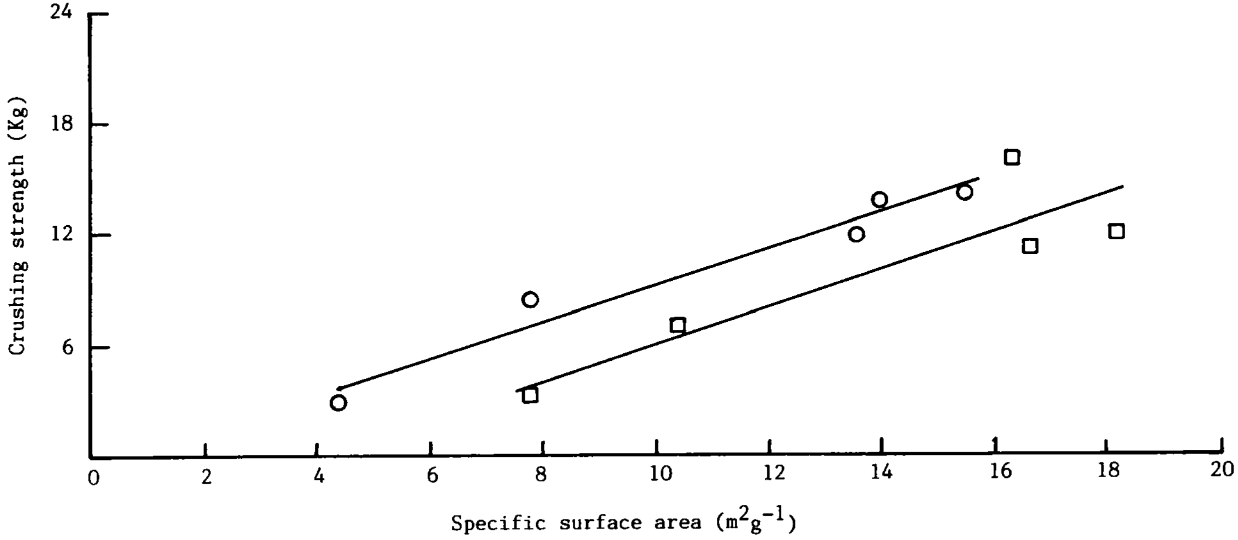


FIGURE 6

The effect of specific surface area on the crushing strength of magnesium carbonate compacts at 50 MNm^{-2}. (Symbols as in Figure 5)

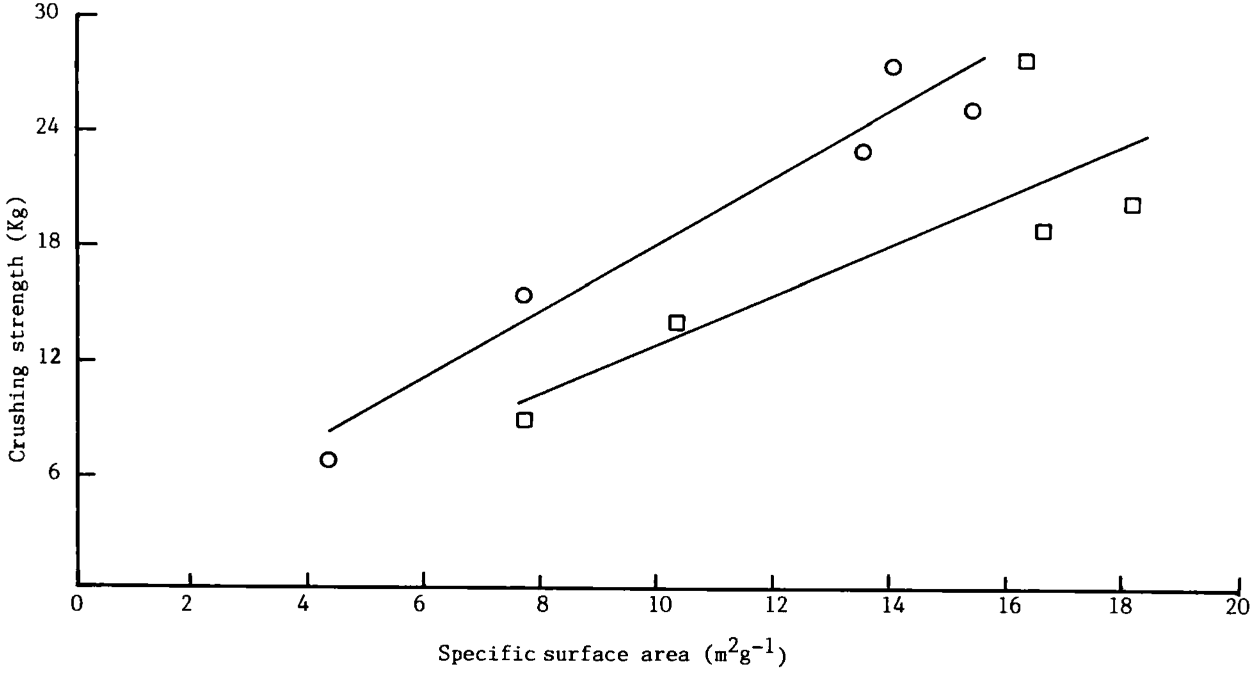


FIGURE 7

The effect of specific surface area on the crushing strength of magnesium carbonate compacts at 99 MNm^{-2}. (Symbols as in Figure 5)

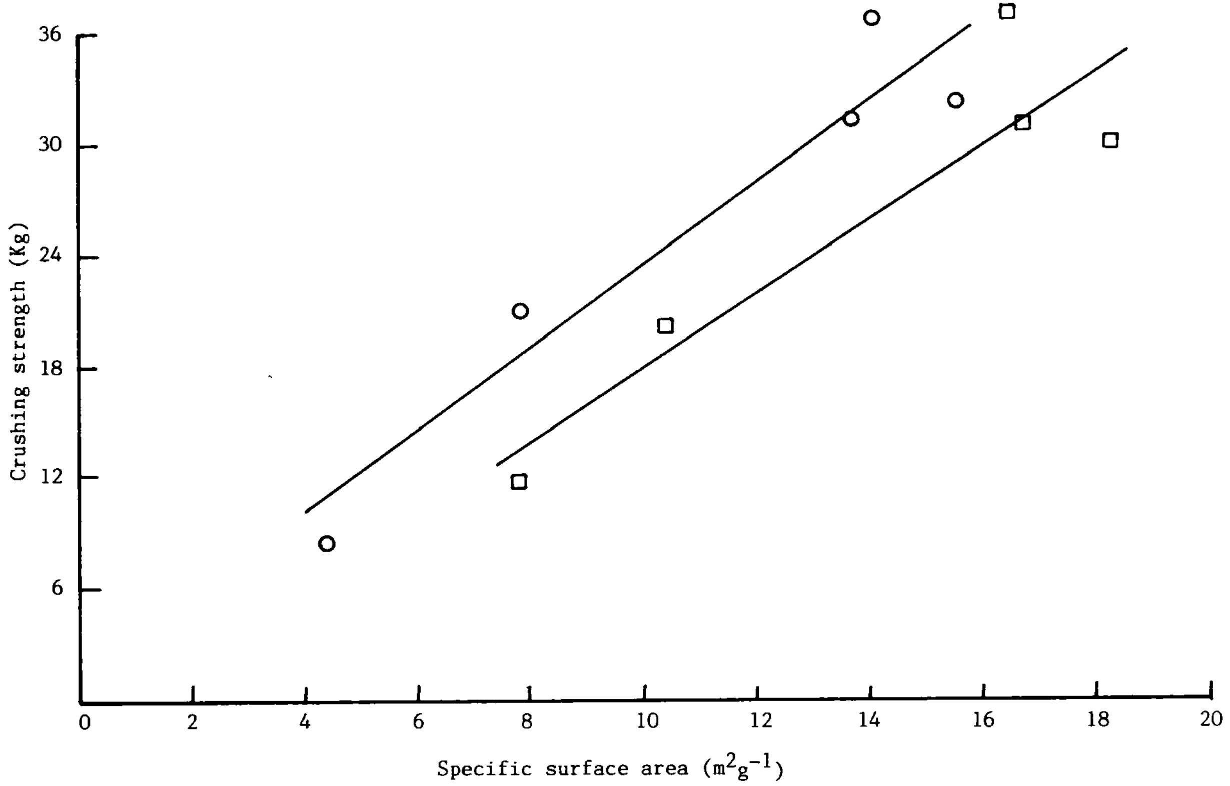


FIGURE 8

The effect of specific surface area on the crushing strength of magnesium carbonate compacts at 148 MNm^{-2}. (Symbols as in Figure 5)

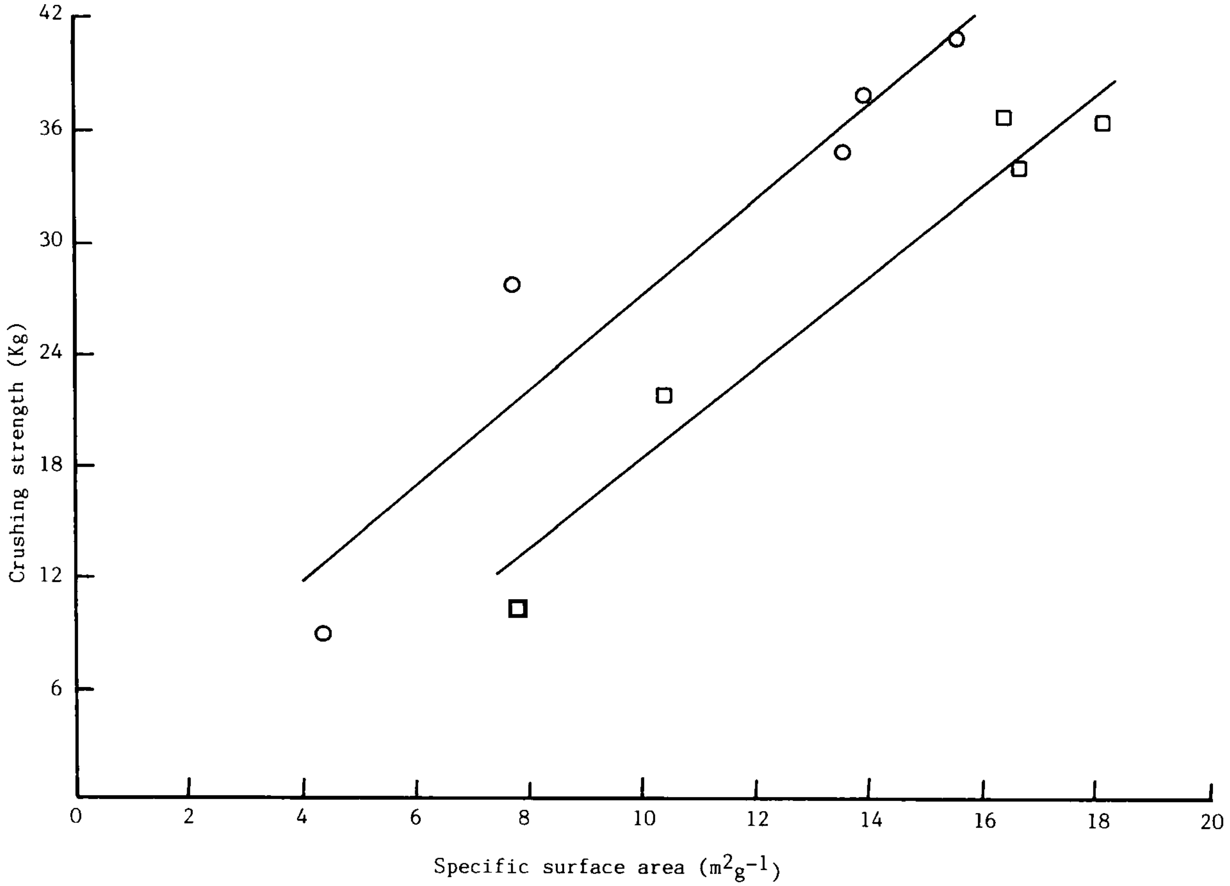


FIGURE 9

The effect of specific surfsce area on the crushing strength of magnesium carbonate compacts at 198 MNm^{-2}. (Symbols as in Figure 5)

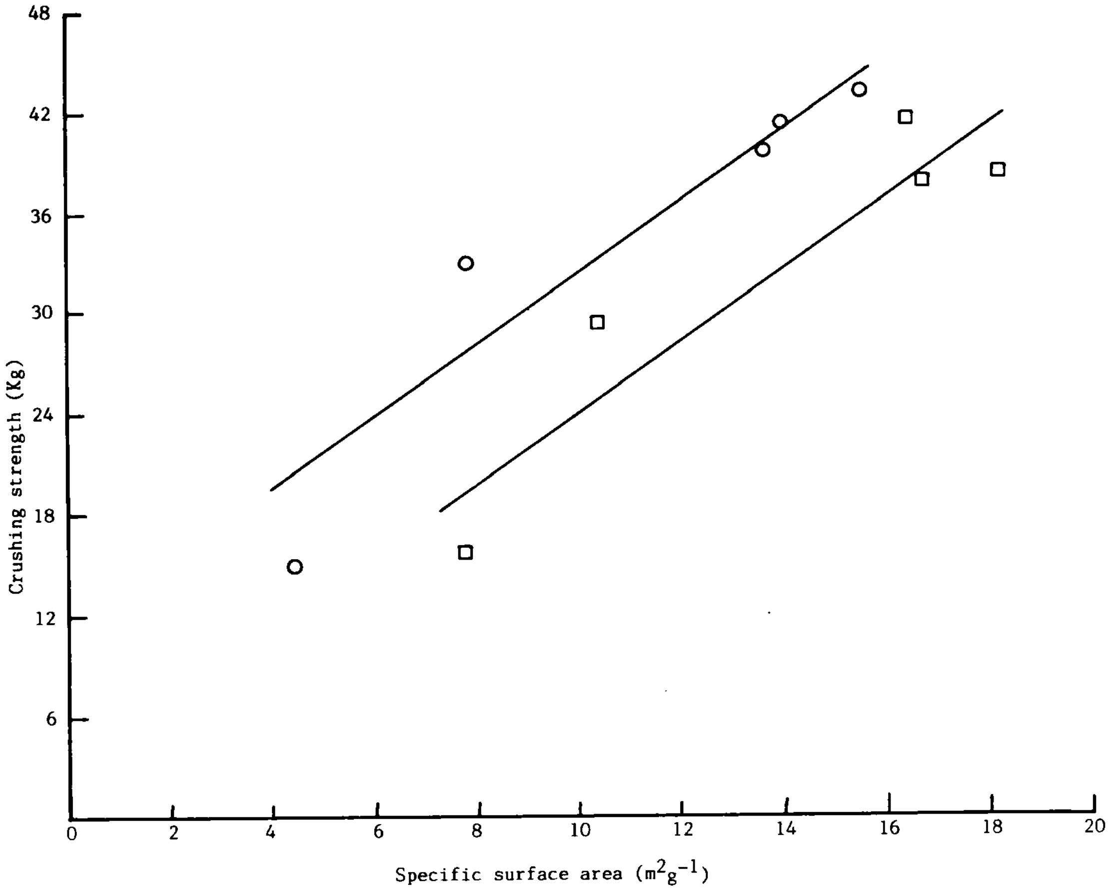


FIGURE 10

The effect of specific surface area on the crushing strength of magnesium carbonate compacts at 248 MNm^{-2}. (Symbols as in Figure 5)

Table 5. The results of linear regression analyses carried out from Figs. 5-10.

Magnesium carbonate		Compression Pressure (MNm^{-2})					
		Powders*	50	99	148	198	248
Granules	Correlation Coefficient $\times 10^{-3}$	982	882	817	906	976	932
	Intercept A $\times 10^{-3}$	-900	-3481	-290	-2426	-6812	2322
	Slope K $\times 10^{-3}$	294	961	1319	2058	2497	2178
Spray dried powders	Correlation Coefficient $\times 10^{-3}$	961	980	970	957	957	917
	Intercept A $\times 10^{-3}$	106	-398	342	532	1441	1099
	Slope K $\times 10^{-3}$	288	960	1758	2293	2577	2165

* For moisture adsorption (%) of magnesium carbonates.

Fell and Newton[13] also showed that for two forms (Crystalline and spray dried) of lactose, the tablet strength increased as the particle size decreased. The influence of particle size (with specific surface area ranging from 11000 to 18600 cm^2/cm^3) on the tableting properties was demonstrated by Hunter[14]. He[14] showed that both of the capping pressure and maximum tablet hardness increased as the specific surface area of primidone increases.

Figures 6-10 show that for both forms of magnesium carbonates, the crushing strength of compacts increases with an increase in the specific surface area of magnesium carbonates. The results of linear regression analyses carried out of the curves from Figures 6-10 are shown in Table 5. The correlation coefficients show a highly significant linear relationship between the specific surface area of magnesium carbonates and the crushing strength of the compacts. The value of slope increases as the compression pressure increases, except for the highest pressure studied (248 MNm^{-2}). This indicates that the rate of increase in crushing strength for magnesium carbonates having a higher value of specific surface area will be more sensitive to the compression pressure (up to 198 MNm^{-2}).

CONCLUSION

The temperature at which magnesium carbonate was prepared had played an important role on the physical properties of the product. The relatively large surface areas of the magnesium carbonates which were prepared at a lower temperature will aid bonding results. Hence, it is postulated that the crushing strength of compacts is correlated to the specific surface area of the magnesium carbonates.

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