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The Effect of Impurities on the Physical Properties of Oxychloride Cements

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THE EFFECT OF IMPURITIES ON THE PHYSICAL PROPERTIES OF OXYCHLORIDE CEMENTS

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The rapidly increasing use of Stucco, a cement made by mixing magnesite with a solution of magnesium chloride, as an exterior for dwelling houses has given rise to an interesting study of its chemical and physical properties. As usually applied, the stucco is made according to the specifications of the Committee on Specifications for Plastic Magnesite, which recommended the following mixture to be standard:

One part by weight of plastic calcined Magnesite
Two parts by weight of Standard Ground Silica
Five parts by weight of Standard Ottawa Sand

This is then mixed with a 22 degree Baume solution of magnesium chloride to the proper consistency. Various colored oxides may be added to color the cement as desired. The cementing properties of such mixture are due to the formation of an oxychloride compound of magnesium by the interaction between magnesite and the magnesium chloride solution, the sand acting only as a filler or as an attachment for the cement crystals.

Plastic calcined magnesite is made by calcining, usually in a rotary kiln, the finely ground Magnesite, a magnesium carbonate mineral occuring chiefly in San Benito county, California, and Stevens county, Washington. It is usually associated with Degomite, a double calcium magnesium carbonate, and with small quantities of silica and oxides of iron and aluminium. Upon such calcination these carbonates are converted to the corresponding oxides.

Inasmuch as calcium oxide does not form an oxychloride cement of very great strength the presence of lime as such in the calcined product has been suggested as one of the causes responsible for the wide variation in strength of different samples of the Stucco. This work was undertaken, (1) to determine the effect of those substances usually associated with magnesite upon the physical properties of the resulting cement, (2) the thermal coefficient of expansion, (3) the linear change during set, (4) rate of solution of the soluble portions of the cement, and (5) the effect of varying the standard mix. The physical properties considered were tensile strength and the cross breaking strength.

Six samples of commercial magnesite were used, to which were added varying amounts of lime, calcium carbonate and the oxides of iron and aluminium. The samples were made up according to Standard Specifications, allowed to stand in the moulds eight hours before removing, stored in the laboratory and broken at intervals of seven, fourteen and twenty-eight days. The average of three or more samples was taken as the result. The tensile strength samples were made up in the usual briquette form and broken in a standard Fairbanks Morse Cement Testing Machine. The cross breaking strength was determined by means of the apparatus shown in figure 1, the bars being twenty inches long,

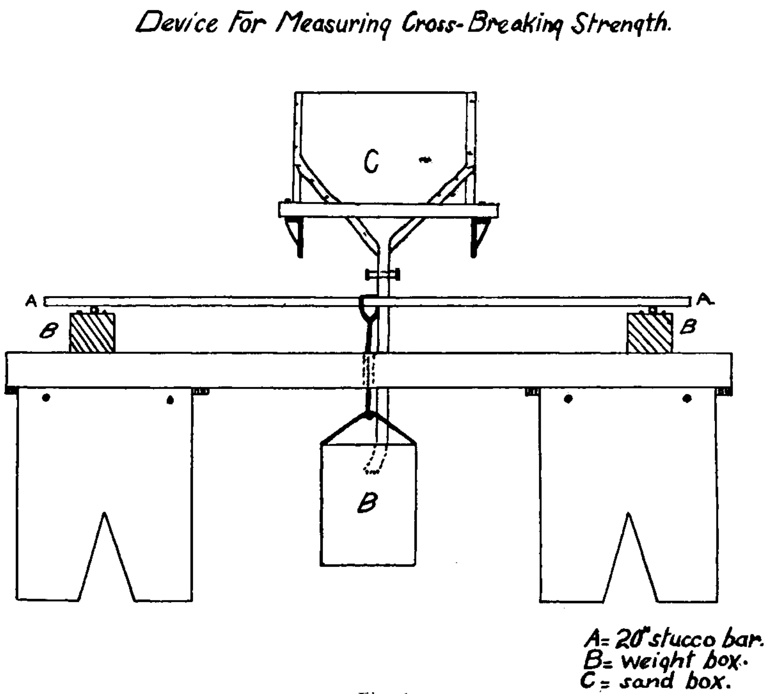

Fig. 1

two inches wide and one half inch thick. These were made up in wooden moulds lightly oiled with cottonseed oil. The cross-breaking strength was calculated as;

$$F = \frac{3WL}{BH}$$

where

F—Cross breaking strength
W—Load applied
B—Width of the bar
L—Length of bars between centers
H—Thickness of the bar

For the bars used F—60w or the cross breaking strength was 60 times the load applied.

The coefficient of expansion and change during set were determined by means of an apparatus designed in this laboratory, shown in figure 2 The microscopes were fitted with micrometer

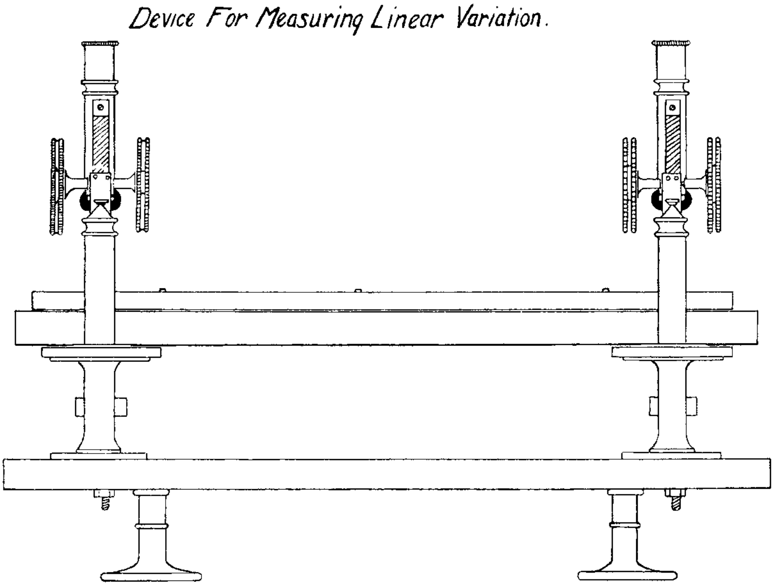

Fig. 2

eye pieces and were firmly mounted five hundred millimeters apart from center to center. The bars were placed on suitable supports and on each end were embedded glass plates marked with cross hairs directly under the objectives. The apparatus was very sensitive to small changes and was capable of determining with low power lenses changes of two hundredths of one per cent.

EXPERIMENTAL RESULTS

Table I (below) shows the analysis of the six different magnesites used in the work. They were taken from different shipments at intervals throughout a year and show a decided variation in composition. The water soluble CaO was determined by slaking a sample in distilled water for twenty-four hours and titrating an aliquot part of the filtrate using both phenolphthalein and methyl orange as indicators. By using both indicators it was possible to determinate the amount of water soluble carbonate present. This varied from 0 in sample C to 0.4 per cent in sample A.

TABLE I

Sample	Specific Gravity	Loss on Ignition	Insoluble Matter	Water Soluble CaO	Al_2O_6 Fe_2O_3	Total CaO	Total MgO
A	1.845	4.62	10.93	1.50	4.67	4.95	74.33
B	1.8115	4.96	11.40	0.80	3.40	4.40	75.83
C	1.745	3.41	6.40	0.81	4.60	5.02	80.75
D	1.803	4.32	9.62	0.93	4.72	4.53	75.62
E	1.816	3.97	8.97	0.89	3.97	4.47	79.30
F	1.873	4.08	6.59	1.22	4.02	4.69	81.36

Table II gives the tensile and cross breaking strengths of the six magnesites made up according to standard mix, that is, one part magnesite, two parts silex and five parts sand made up to the proper consistency with 22° Baume solution of magnesium chloride. The results show a wide variation of strengths and also different rates of increasing strength with age.

TABLE II

Sample	Tensile Strength			Cross Breaking Strength		
	7 Day	14 Day	28 Day	7 Day	14 Day	28 Day
A	625	632	754	1252	1623	1741
B	475	568	519	1292	1246	1287
C	638	605	654	1101	1462	1456
D				1200	1890	1818
E	628	663	769	1165	1492	1760
F	720	800	814	1288	1535	1610

It has been observed that calcium carbonate has little effect upon the strength of stucco and has been added to the mix, finely ground, as a filler. A patent has been issued based upon this fact under the terms of which the raw magnesite is calcined to a temperature supposed to convert the magnesium carbonate to the oxide, but not enough to change the calcium carbonate to lime. Table III shows the effect of adding finely ground calcite to the mix, the amount added, calculated as percentage of magnesite. These results are plotted in figure 3 in which the strength of the neat mix i. e., no carbonate added, is taken as unity and the strength of the samples to which the carbonate was added calculated as:

$$\frac{\text{Strength of sample}}{\text{Strength of neat mix}}$$

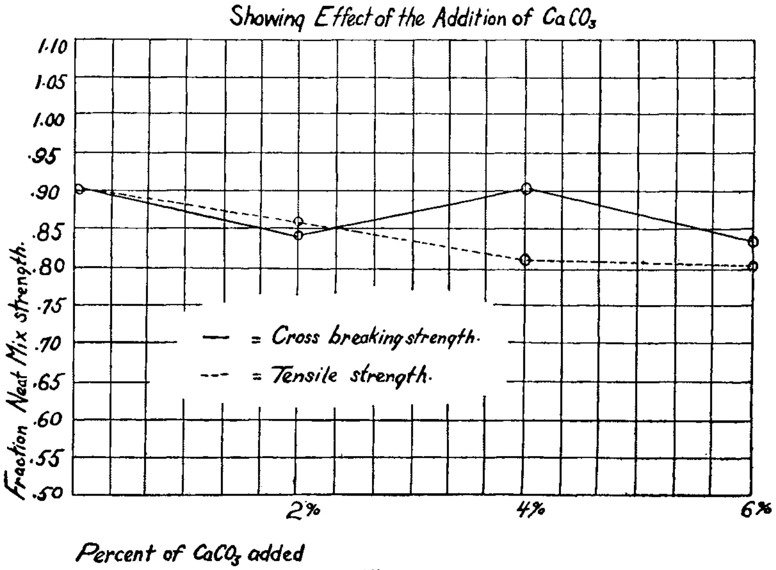

Fig. 3

The figures so obtained were all averaged together for 7-day, 14-day, and 28-day samples, and plotted as ordinates with the percentage calcium carbonate as abscissa. The curve shows comparatively little change for either cross breaking or tensile strength.

TABLE III

Sample	$CaCO_3$ Added Per cent	Tensile Strength			Cross Breaking Strength		
		7 Day	14 Day	28 Day	7 Day	14 Day	28 Day
A	0	625	632	754	1252	1623	1741
B	2	499	578	715	896	1496	1539
B	4	487	547	745	1206	1577	1628
B	6	510	520	648	1000	1297	1410
D	0	638	605	654	1101	1462	1456
D	2	545	633	791	1226	1381	1453
D	4	465	652	711	1161	1510	1724
C	6	536	602	710	1100	1492	1699

Table IV shows the effect of adding the oxides of aluminium and of iron. The oxides were prepared by burning the precipita-

TABLE IV

Sample	Material Added	Tensile Strength			Cross Breaking Strength		
		7 Day	14 Day	28 Day	7 Day	14 Day	28 Day
A	0	625	632	754	1252	1620	1740
A	2 per cent Fe_2O_3	570	795	745	1200	1500	1650
A	4 per cent Fe_2O_3	515	780	764	1250	1400	1550
A	4 per cent Al_2O_3	540	732	762	1330	1500	1560

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ted hydroxide and grinding to a degree of fineness approximating that of the magnesite. The results show very little effect due to the presence of the oxides. The iron colored the samples decidedly.

In Table V are the results obtained by the addition of lime. The ordinary calcium oxide used in the laboratory was ground very fine and kept in a dry place during this phase of the work. As it had been suggested that the failure of many stuccos was due to the presence of excessive amounts of lime this part of the work was given special consideration. The results are shown graphically in figure 4 in which the strength of the neat mix is taken as

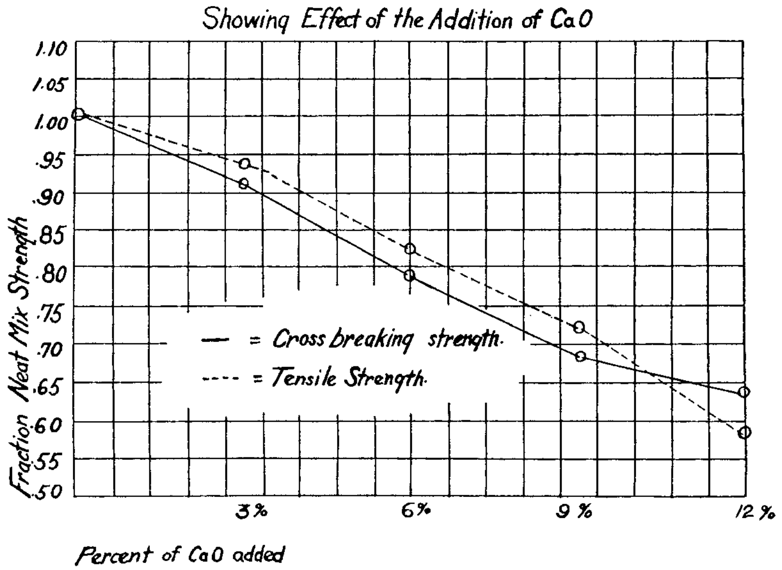

Fig. 4

unity and the strength of the samples to which lime was added calculated as in figure 3. The decrease in strength is decided. Other investigators have reported far greater deviations than the following table shows; however it may be worth mentioning that in each case the mix was made up to the same degree of consistency rather than keeping the amount of magnesium chloride solution constant. An appreciably greater amount of solution was necessary in case of the high lime samples. Considering the widely divergent nature of the two tests the two curves show a remarkable agreement.

Table VI shows the coefficient of linear expansion throughout ranges of temperature commonly experienced in moderate climates. The average is only slightly deviated from in the different sam-

TABLE V

Sample	CaO Added Per cent	Tensile Strength			Cross Breaking Strength		
		7 Day	14 Day	28 Day	7 Day	14 Day	28 Day
C	0	638	605	654	1101	1462	1456
C	1	570	707	699	1006	1517	1650
C	2	338	575	586	1090	1243	1444
C	4	479	573	747	962	1386	1309
C	10	395	430	400	690	960	900
D	0				1200	1890	1818
D	3				1160	1470	1628
D	6				1170	1218	1250
D	9				945	970	1065
D	12				975	1031	1100
E	0	628	663	709	1165	1493	1760
E	3	603	650	680	1070	1410	1600
E	6	537	600	605	1065	1317	1430
E	9	550	590	580	928	1017	1129
E	12	360	405	502	803	932	1020
F	0	620	800	814	1188	1535	1610
F	3	639	722	765	1225	1425	1560
F	6	597	595	630	1025	1215	1392
F	9	485	500	590	908	1029	1190
F	12	378	428	450	760	908	1002

ples, being a little greater than that of iron . The addition of lime seemed to have little effect on this value.

TABLE VI

Sample	Mix	Thermal Range Degrees Centigrade	Coefficient of Expansion
1	neat	41—24	0.0000175
2	neat	44—27	0.0000141
3	neat	36—28	0.0000150
4	neat	40—27	0.0000154
5	neat	44—4	0.0000140
6	3 per cent CaO add.	48—29	0.0000147
7	6 per cent CaO add.	51—35	0.0000150
8	6 per cent CaO add.	50—34	0.0000150
9	9 per cent CaO add.	43—22	0.0000147
10	9 per cent CaO add.	45—17	0.0000152

Calculated on a basis of a ten foot wall which would represent a moderate extreme of stucco space, throughout a range of temperature commonly experienced in this climate the linear change would be nine hundredths of an inch.

Table VII shows a more possible cause of stucco cracking during set than the decrease of strength with increased lime content. The presence of added lime increased the shrinkage over ten times. The samples were made up in the moulds used for determining the linear change with change of temperature and placed at once under the microscopes. Readings were taken at intervals of two hours for twelve hours and then twice daily for four days. The contraction was rapid at the beginning of the set, practically the entire change taking place in the first six hours. The second and third day showed very little change in the bar and the fourth day no change at all.

TABLE VII

Change of Length During Set		Percentage of Linear Change
Sample	Composition	
1	neat	0.004
2	neat	0.0035
3	neat	0.0035
4	3 per cent CaO Added	0.020
5	3 per cent CaO Added	0.022
6	6 per cent CaO Added	0.036
7	6 per cent CaO Added	0.034
8	9 per cent CaO Added	0.043

The above results suggested trying the behavior of pats of cement made up one half-inch thick at the center, tapering to a thin edge, the pat being two and one-half inches in diameter. Varying amounts of lime were added to these pats, which were then mounted on oiled glass plates. Three of each mix were made up and allowed to stand in the laboratory. The cracks at the edges of the pat extended toward the center and occurred within six hours. Table VIII shows these results.

TABLE VIII

Sample	Composition Percentage of CaO	Sound	Cracked
I	neat	2	1
	3	1	2
	6	3	0
	9	0	3
II	3	1	2
	6	1	2
	9	0	3
III	3	1	2
	6	1	2
	9	0	3

When stucco is used as an exterior covering it is obvious that solution by rainfall would be an important factor. To determine the amount so dissolved and the rate of solution the following method was devised. Samples of different mix were allowed to age in the laboratory for thirty to forty days, weighed and immersed in water bath. At intervals of 24, 48, 72, 96, 120 and 144 hours they were taken from the bath, wiped dry and quickly weighed. After the final weighing, that is after 144 hours, the sample was dried to constant weight by standing in the laboratory, and re-weighed. These results in Table IX show an increase of weight due to absorbed water up to 24 hours. A decrease in wieght then occurred due to solution of some part of the stucco, rapidly at first, but becoming almost zero after 120 hours.

TABLE IX

Sample	Composition			Tensile Strength	Percentage Increase in Weight						Loss by Solution
	MgO	Silex	Sand		24 Hrs.	48 Hrs.	72 Hrs.	96 Hrs.	120 Hrs.	144 Hrs.	
B_6	15	25	60	843	4.973	4.629	4.231	3.969	3.817	3.795	5.486
B_7	12.5	27.5	60	733	4.669	4.405	4.006	3.776	3.680	3.427	4.737
B_8	12.5	32.5	55	882	4.929	4.674	4.272	4.140	3.882	3.815	4.375
B_9	12.5	37.5	50	749	5.091	4.905	4.637	4.307	4.326	4.243	4.046

These results are shown in figure 5. The percentage increase in weight is plotted on the left side of the curve and the total loss by solution on the right side. The curve shows that most water was absorbed by B_9, which contained the largest percentage of silex but it also lost the least by solution. B_6 which contained the least silex lost the most by solution. It appears that the variation of

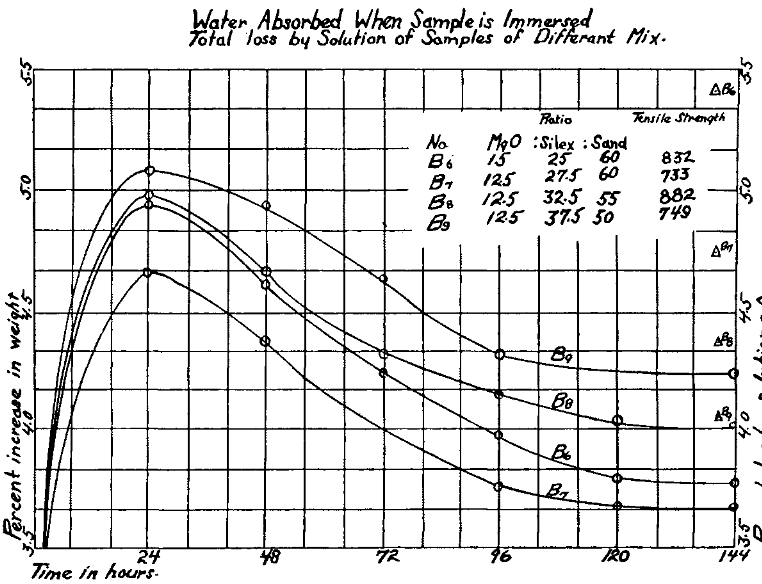

Fig. 5

the amount of silex has an effect on the amount of material dissolved out of the cement as the position of the samples in the figure is in inverse ratio to the amount of silex present.

In figure 6 are shown the results obtained by varying the mix both ways from the standard. In series I the magnesite of each mix is kept constant at 12.5 per cent and the remainder is divided

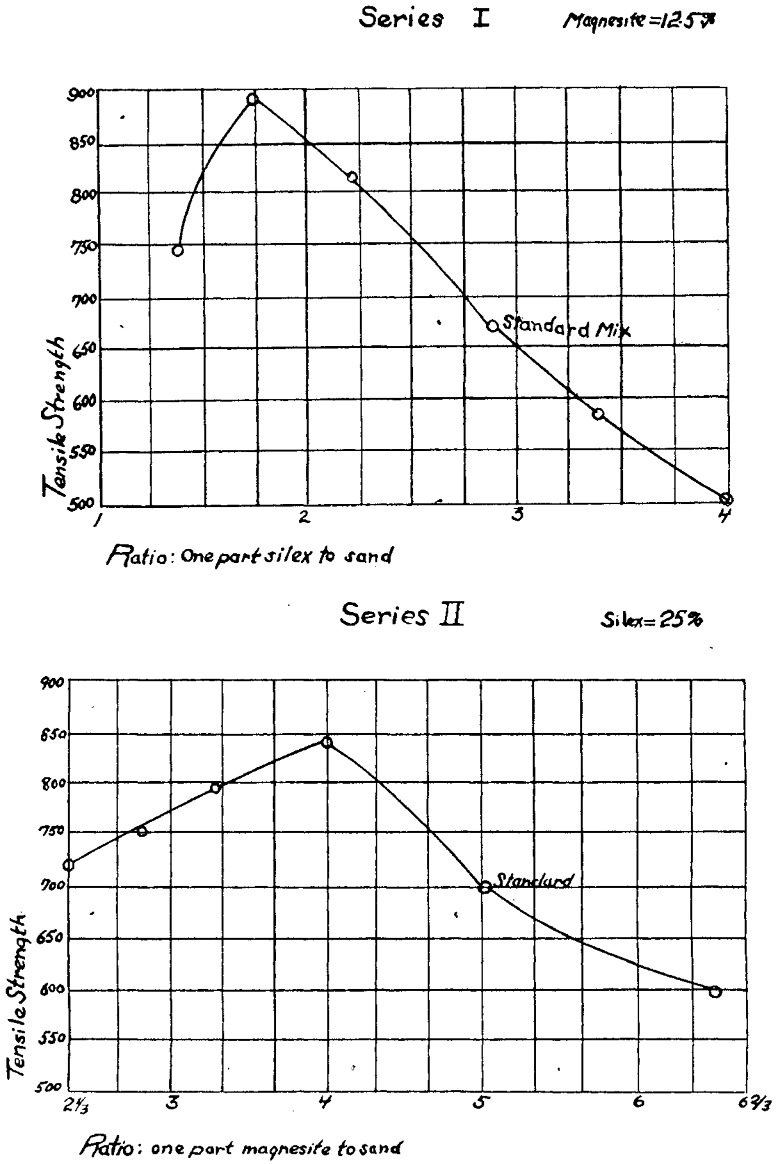

Fig. 6

between silex and sand in the ratio indicated. In series II the silex is kept constant at 25 per cent of the total mix and the remainder is divided between magnesite and sand in the ratio indicated. The results show the greatest tensile strengths at 14 days in samples consisting of 12.5 per cent magnesite, 32.5 per cent silex and 55 per cent sand; and 15 per cent magnesite, 25 per cent silex and 60 per cent sand. These vary somewhat from the standard mix, in each case the greatest strength being at a mix with a less amount of sand than the standard.

CONCLUSIONS AND SUMMARY

As the results of the investigation as covered in this work it may be concluded:

(1) That the presence of small amounts of lime has but little detrimental effect on the strength of the cement. Although this is not in strict accord with results obtained by other investigators, the suggestion might be made that the nature of the lime added i. e. the degree of hydration, fineness, etc., may be of vital importance.

(2) That the presence of oxides of iron and aluminium and of calcium carbonate when finely ground has no effect upon the strength of the stucco beyond the obvious dilution of the active principle.

(3) That the change of volume due to temperature changes is so small that no undue strains would be brought to bear upon the cement when used as an exterior stucco throughout ranges of temperature experienced in this country.

(4) That the mix giving highest tensile strength is very nearly 12.5 parts magnesite, 32.5 parts silex and 55 parts sand.

(5) That the cracking of stucco of high lime content can be more properly laid to the volume changes occurring during set rather than to the weakening effect of the lime upon the tensile or cross breaking strengths.

(6) That the average of the tensile and cross breaking strengths stands in the following ratio:

(1) 7 day cross breaking strength = 1.98 times tensile strength
(2) 14 day cross breaking strength = 2.23 times tensile strength
(3) 28 day cross breaking strength = 2.28 times tensile strength

II

Calcium carbonate and the oxides of iron and aluminium when present up to the limiting amount possible in calcined magnesite have little appreciable effect on the properties of the stuccos.

The calcium oxide present derived from the decomposition of the calcium carbonate during calcination of the magnesite, lowers the tensile and cross breaking strengths of the stucco approximately one per cent for each three per cent of lime present.

The coefficient of thermal expansion of the standard stucco mix is very nearly 0.00001506.

The change in volume during set is negative and is increased decidedly by the presence of lime.

The greatest strength is obtained by mixing the magnesite, silex and sand in approximately the ratio of one part magnesite, two parts silex and four parts sand.

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