CHAPTER 7

EXPERIMENTAL RESULTS

7.1 Chemical Analysis of Raw Materials

The chemical analyses of limestone, spent shale and clay are presented in table 7.1.

Table 7.1 Chemical composition of raw materials.

Raw Materials	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	L.O.I.
limestone	1.78	0.65	0.40	53.70	0.91	0.10	trace	42.46
spent shale	41.77	14.67	3.90	17.16	7.78	2.32	1.21	11.19
clay	66.54	15.67	5.08	1.46	2.05	1.95	0.30	6.95

7.2 Proportions

Proportions wereobtained by graphical determination. The proportions of two component mixtures are shown in table 7.2 and the proportions of three component mixtures are shown in table 7.3.

Table 7.2 Proportions of two-component mixtures

Sample No.	limestone (%)	spent shale (%)
1	71.57	28.43
2	70.78	29.22
3	69.99	30.01
4	69.20	30.80

Table 7.2 (Cont.)

Sample No.	limestone (%)	spent shale (%)
5	68.40	31.60
6	67.59	32.41
7	66.77	33.23
8	65.95	34.05
9	65.13	34.87
10	64.29	35.71

Table 7.3 Proportions of three-component mixtures.

Sample No.	spent shale (%)	limestone (%)	clay (%)
1	34.99	64.17	0.84
2	33.63	66.36	0.01
3	33.09	65.28	1.63
4	31.75	67.46	0.79
5	31.50	66.91	1.59
6	31.24	66.37	2.39
7	30.99	65.82	3.19
8	30.73	65.27	4.00
9	30.17	69.06	0.77
10	29.94	68.52	1.54
11	29.70	67.98	2.32
12	29.46	67.44	3.10
13	29.22	66.89	3.89
14	28.98	66.34	4.68
15	28.61	70.64	0.75
16	28.39	70.11	1.50
17	28.17	69.57	2.26
18	27.95	69.03	3.02
19	27.73	68.49	3.78
20	27.51	67.94	4.55
21	27.29	67.39	5.32
22	27.06	66.83	6.11
23	27.07	72.20	0.73
24	26.87	71.67	1.46
25	26.67	71.14	2.19
26	26.47	70.60	2.93
27	26.26	70.06	3.68
28	26.06	69.52	4.42
29	25.85	68.97	5.18
30	25.65	68.42	5.93
31	25.44	67.86	6.70
32	25.23	67.30	7.47
33	25.36	73.22	1.42
34	25.18	72.69	2.13
35	25.00	72.15	2.85
36	24.81	71.61	3.58
37	24.62	71.07	4.31
38	24.43	70.53	5.04
39	24.24	69.98	5.78
40	24.05	69.43	6.52
41	23.86	68.88	7.26
42	23.67	68.32	8.01

Table 7.3 (Cont.)

Sample No.	spent shale (%)	limestone (%)	clay (%)
43	23.54	73.68	2.78
44	23.38	73.14	3.48
45	23.20	72.61	4.19
46	23.03	72.07	4.90
47	22.86	71.52	5.62
48	22.68	70.98	6.34
49	22.51	70.42	7.07
50	22.33	69.87	7.80
51	22.15	69.32	8.53
52	21.97	68.76	9.27
53	21.88	74.39	3.73
54	21.72	73.85	4.43
55	21.56	73.32	5.12
56	21.40	72.77	5.83
57	21.24	72.23	6.53
58	21.08	71.68	7.24
59	20.92	71.13	7.95
60	20.76	70.57	8.67
61	20.59	70.02	9.39
62	20.43	69.45	10.12
63	20.26	68.89	10.85
64	20.12	74.55	5.33
65	19.98	74.01	6.01
66	19.83	73.47	6.70
67	19.68	72.92	7.40
68	19.54	72.37	8.09
69	19.39	71.82	8.79
70	19.24	71.26	9.50
71	19.09	70.70	10.21
72	18.94	70.14	10.92
73	18.78	69.58	11.64
74	18.52	74.95	6.53
75	18.38	74.41	7.21
76	18.25	73.87	7.88
77	18.11	73.32	8.57
78	17.97	72.77	9.26
79	17.84	72.21	9.95
80	17.70	71.66	10.64
81	17.56	71.10	11.34
82	17.42	70.53	12.05
83	17.28	69.96	12.76
84	17.09	75.83	7.03

Table 7.3 (Cont.)

Sample No.	spent shale (%)	limestone (%)	clay (%)
85	16.97	75.34	7.69
86	16.85	74.80	8.35
87	16.72	74.26	9.02
88	16.60	73.70	9.70
89	16.47	73.15	10.38
90	16.35	72.59	11.06
91	16.22	72.04	11.74
92	16.09	71.47	12.44
93	15.97	70.90	13.13
94	15.84	70.33	13.83
95	15.59	72.26	8.15
96	15.48	75.72	8.80
97	15.36	75.18	9.46
98	15.25	74.63	10.12
99	15.14	74.08	10.78
100	15.03	73.52	11.45
101	14.91	72.96	12.13
102	14.80	72.40	12.80
103	14.68	71.83	13.49
104	14.57	71.26	14.17
105	14.14	76.63	9.23
106	14.04	76.09	9.87
107	13.94	75.54	10.52
108	13.84	74.99	11.17
109	13.74	74.43	11.83
110	13.64	73.87	12.49
111	13.53	73.32	13.15
112	13.43	72.75	13.82
113	13.32	72.18	14.50
114	13.22	71.61	15.17
115	12.75	76.98	10.27
116	12.66	76.44	10.90
117	12.57	75.89	11.54
118	12.48	75.33	12.19
119	12.39	74.78	12.83
120	12.29	74.22	13.49
121	12.20	73.66	14.14
122	12.11	73.09	14.80
123	12.01	72.52	15.47
124	11.92	71.94	16.14
125	11.49	77.87	10.64
126	11.41	77.32	11.27

Table 7.3 (Cont.)

Sample No.	spent shale (%)	limestone (%)	clay (%)
127	11.33	76.77	11.90
128	11.25	76.22	12.53
129	11.17	75.67	13.16
130	11.08	75.11	13.81
131	11.00	74.55	14.45
132	10.92	73.98	15.10
133	10.83	73.42	15.75
134	10.75	72.84	16.41
135	10.66	72.27	17.07
136	10.19	78.20	11.61
137	10.12	77.65	12.23
138	10.05	77.10	12.85
139	9.97	76.55	13.48
140	9.90	75.99	14.11
141	9.83	75.43	14.74
142	9.75	74.87	15.38
143	9.68	74.30	16.02
144	9.60	73.73	16.67
145	9.53	73.15	17.32
146	9.45	72.58	17.97
147	8.93	78.51	12.56
148	8.87	77.96	13.17
149	8.80	77.41	13.78
150	8.74	76.86	14.40
151	8.68	76.30	15.02
152	8.61	75.74	15.65
153	8.55	75.17	16.28
154	8.48	74.61	16.91
155	8.42	74.03	17.55
156	8.35	73.46	18.19
157	8.29	72.88	18.83
158	7.71	78.82	13.47
159	7.66	78.27	14.07
160	7.60	77.72	14.68
161	7.55	77.16	15.29
162	7.50	76.60	15.90
163	7.44	76.04	16.52
164	7.39	75.47	17.14
165	7.33	74.90	17.77
166	7.27	74.33	18.40
167	7.22	73.75	19.03
168	7.16	73.17	19.67

Table 7.3 (Cont.)

Sample No.	spent shale (%)	limestone (%)	clay (%)
169	6.54	79.12	14.34
170	6.49	78.57	14.94
171	6.45	78.01	15.54
172	6.40	77.45	16.15
173	6.36	76.89	16.75
174	6.31	76.33	17.36
175	6.26	75.76	17.98
176	6.21	75.19	18.60
177	6.17	74.61	19.22
178	6.12	74.03	19.85
179	6.07	73.45	20.48
180	5.40	79.41	15.19
181	5.37	78.85	15.78
182	5.32	78.30	16.38
183	5.29	77.74	16.97
184	5.25	77.17	17.58
185	5.21	76.61	18.18
186	5.17	76.04	18.79
187	5.13	75.46	19.41
188	5.10	74.88	20.02
189	5.06	74.30	20.64
190	4.30	79.69	16.01
191	4.27	79.13	16.60
192	4.24	78.57	17.19
193	4.21	78.01	17.78
194	4.18	77.44	18.38
195	4.15	76.88	18.97
196	4.12	76.30	19.58
197	4.09	75.73	20.18
198	4.06	75.15	20.79
199	4.03	74.56	21.41
200	3.26	80.51	16.23
201	3.24	79.95	16.81
202	3.21	79.40	17.39
203	3.19	78.84	17.97
204	3.17	78.27	18.56
205	3.15	77.71	19.14
206	3.12	77.14	19.74
207	3.10	76.56	20.34
208	3.08	75.99	20.93
209	3.05	75.41	21.54
210	3.03	74.82	22.15

Table 7.3 (Cont.)

Sample No.	spent shale (%)	limestone (%)	clay (%)
211	2.22	80.77	17.01
212	2.21	80.21	17.58
213	2.19	79.66	18.15
214	2.17	79.10	18.73
215	2.16	78.53	19.31
216	2.15	77.96	19.89
217	2.13	77.39	20.48
218	2.11	76.82	21.07
219	2.10	76.24	21.66
220	2.08	75.66	22.26
221	2.06	75.07	22.87

*Further details of the proportions in table 7.2 and 7.3 such as % oxide in clinker, phase compositions and their moduli values are given in appendix C.

Sample no. 35 from table 7.3 was chosen to produce cement by firing nodules of about 1 cm in diameter in the electrical muffle kiln at 1400°C for one hour. The firing procedure was the same as in the preliminary investigation.

7.3 X-ray Examination of Cement Powder

7.3.1 Qualitative Analysis

According to the x-ray patterns (Figure 7.1) of the cement from spent shale, most of the peaks had d-spacings between 3.1 and 2.6°A (29-34° 2θ for CuKα radiation). They were 3.05, 2.78, 2.76 and 2.61°A. The x-ray d-spacings depart slightly from those given in the literature

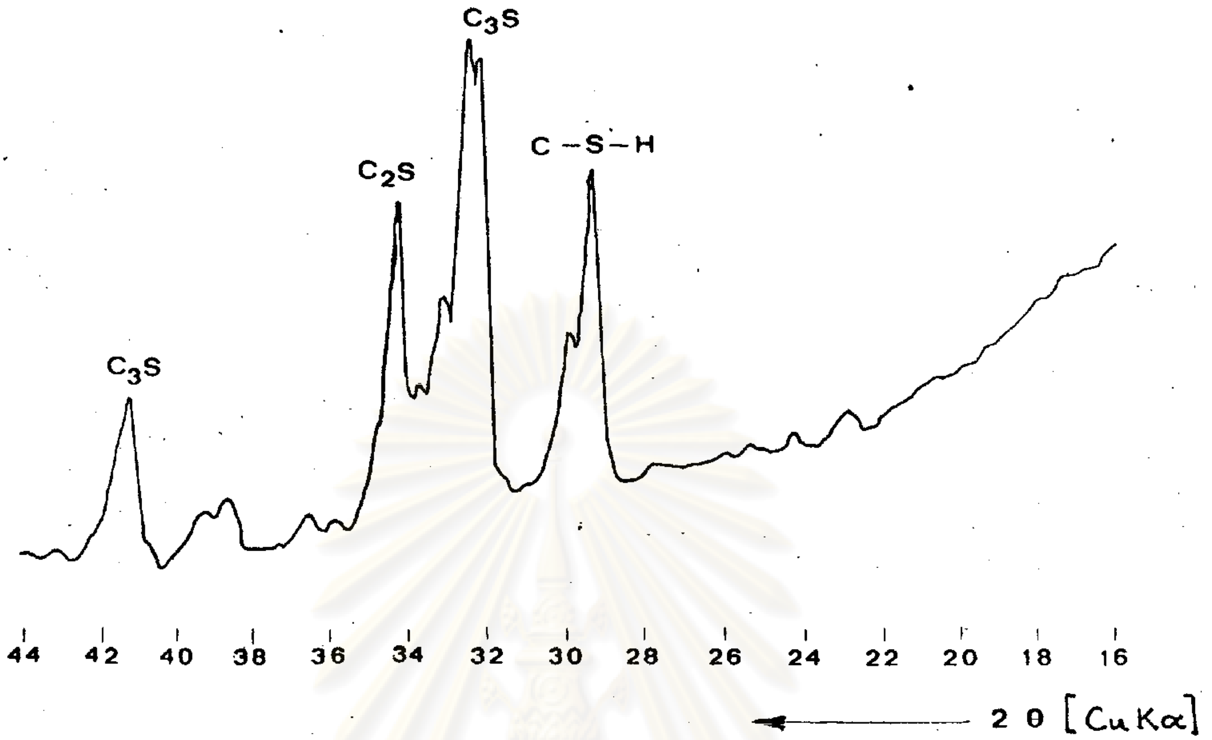


FIGURE 7.1 X-RAY DIFFRACTION PATTERN OF CEMENT FROM SPENT SHALE

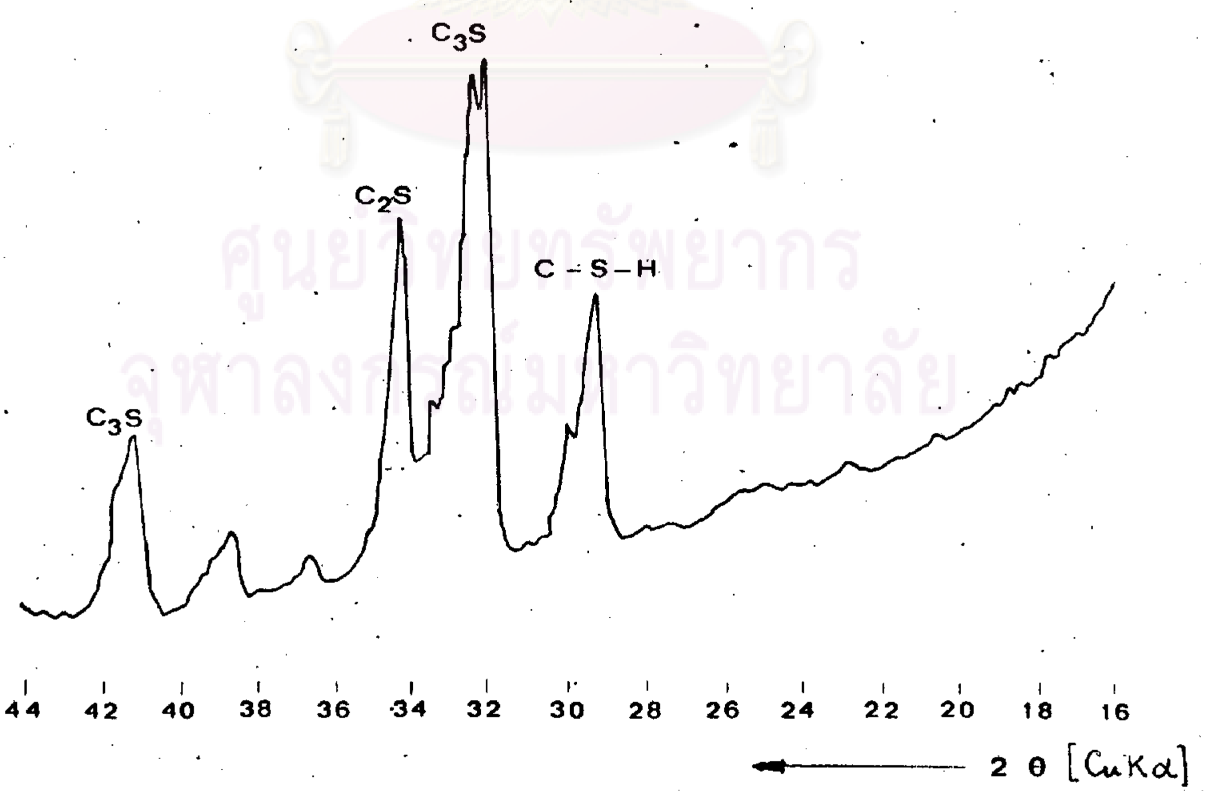


FIGURE 7.2 X-RAY DIFFRACTION PATTERN OF ELEPHANT BRAND CEMENT

(appendix D). Midgley and Fletcher[19] suggested that the shift might be due to the presence of lines from other products at about the same spacing. Hence, the phase compositions could be identified. Difficulties occurred at the line 2.78^{o}A because the value for d-spaciugs of C_3S is 2.776^{o}A and for d-spacings of C_2S is 2.778^{o}A, which are very close together. Yannaquis[27] deduced that because of superposition of the stronger lines, the identification of C_2S in the presence of C_3S could only be made on lines of medium intensity. Thus, the 2.78^{o}A line was indicative of C_3S.

Consequently, all the peaks of the x-ray diffraction patterns could be broadly assigned to β-C_2S, C_3S, C_3S (alite) and C-S-H, as summarized in table 7.4.

Table 7.4 Identification of the phases.

Bragg Angle 2Θ	d (^{o}A)	Identifed Compound
29.30	3.05	C-S-H
32.10	2.78	C_3S
32.40	2.76	alite (C_3S)
34.30	2.61	β-C_2S

The Elephant brand cement which was selected as the representative of the commercial Portland cement type I, was subjected to x-ray diffraction. All the peaks obtained (Figure 7.2), under the same conditions, for C_3S, β-C_2S and C-S-H resembled the cement from spent shale but their intensities differed.

7.3.2 Quantitative Analysis

The quantitative estimation of the phases, using x-ray diffraction, is based on the fact that the integrated intensity of a reflection is directly proportional to the amount of the substance producing it. The x-ray peak intensities were measured corresponding to:

C-S-H	3.05 °A
C_3S	2.78, 2.76 °A
β-C_2S	2.61 °A

From equation 6.2 $I\alpha/I\alpha\rho = W\alpha$,

The results of the quantitative estimation of phases of both types of cement are given in table 7.5.

Table 7.5 The quantitative estimation of phases.

Sample	C_3S	β-C_2S	C-S-H
cement from spent shale (C_{ss})	12.10	4.20	4.25
Elephant brand cement (C_{ELE})	13.05	4.75	3.25
$\frac{I\alpha}{I\alpha\rho} = \frac{I_{ss}}{I_{ELE}}$	0.93	0.88	1.31

Comparing C_{ss} and C_{ELE}:-

C_3S, β-C_2S : $C_{ss} < C_{ELE}$

C-S-H : $C_{ss} > C_{ELE}$

A lower amount of C_3S and C_2S would decrease the strength of the cement. The C_3S of C_{ss} was lower than that of C_{ELE} 7.28% and the C_2S of C_{ss} was lower than that of C_{ELE} 11.58%. This affected strength at the later ages than at the early ages because the lower amount of C_3S was much more significant than the lower amount of C_2S.

The C-S-H of C_{ss} was higher than that of C_{ELE} 30.77%. This was a considerable difference. It implied that cement from spent shale hydrated more quickly than Elephant brand cement.

7.4 Chemical analysis of Cement from spent shale

Table 7.6 The chemical compositions of cement from spent shale, are as follows:

chemical composition	cement from spent shale (%)
SiO_2	20.44
Al_2O_3	5.88
Fe_2O_3	2.58
MgO	2.31
CaO	63.97
K_2O	0.35
Na_2O	0.40
SO_3	2.29
L.O.I.	1.46
Ins. residue	0.30
Free CaO	0.45
Gypsum	4.93

Table 7.6 (Cont.)

chemical composition	cement from spent shale (%)
Calculation:	
C_3S	55.36
C_2S	16.84
C_3A	11.22
C_4AF	7.85
L.S.F.	94.55
L.C.F.	93.86
H.M.	2.21
S.M.	2.42
A.M.	2.28

Table 7.7 Comparison of the Chemical composition of Portland cement type I with other types of Cement

Chemical Composition	%calculation (Raw mix)	cement from spent shale (%)	Elephant brand cement (%)	Payanak brand cement (%)	British cement (%)	American cement (%)	%ASTM[2] (P.C. Type I) &[26] other standards
SiO_2	20.52	20.44	21.63	21.56	21.31	21.53	ave. 21.08*
Al_2O_3	6.90	5.88	5.09	4.24	6.06	5.43	ave. 5.79*
Fe_2O_3	2.12	2.58	2.92	3.93	2.77	2.50	ave. 2.86*
CaO	64.91	63.97	64-66	63.27	64.78	63.88	ave. 63.85*
MgO	4.01	2.31	0.91	1.01	0.86	2.25	max. 5.00
L.O.I.	-	1.46	0.82	1.96	-	-	max. 3.00
Na_2O	0.47	0.40	0.10	-	0.30	0.32	ave. } 1.40
K_2O	1.07	0.35	0.1-0.5	-	0.61	0.63	
SO_3 when $C_3A>8\%$	-	2.29	1.68	2.82	1.91	1.68	max. 3.50
Ins. residue	-	0.30	0.11	0.47	-	-	max. 0.75
Free CaO	-	0.45	≯2	1.11	1.43	1.05	-
Gypsum	-	4.93	4-7	-	-	-	-
C_3S	58.87	55.36	58.00	51.63	45.50	47.25	51.70*
C_2S	14.43	16.84	18.26	22.87	26.67	37.81	21.40*
C_3A	14.71	11.22	8.60	4.48	11.50	10.25	10.50*
C_4AF	6.46	7.85	8.89	11.95	8.50	7.50	8.70*

Table 7.7 (Cont.)

Chemical Composition	%calculation (Raw mix)	cement from spent shale (%)	Elephant brand cement (%)	Payanak brand cement (%)	British cement (%)	American cement (%)	%ASTM [2] (P.C. Type I) & other standards [26]
L.S.F.	97.53	94.55	93.08	90.13	92.29	91.64	{ min. 66.00 max.102.00
L.C.F.	-	93.86	91.62	88.50	90.21	90.10	-
H.M.	2.20	2.21	2.19	2.13	2.15	2.17	1.70-2.20
S.M.	2.27	2.42	2.70	2.64	2.41	2.72	2.40-2.70
A.M.	3.25	2.28	1.74	1.08	2.19	2.17	1.00-4.00

7.5 Physical Properties of Cement from Spent Shale

Following the standard test method of ASTM in appendix B, the results of the physical test of cement from spent shale are as follows:

Table 7.8 Physical characteristics of cement from spent shale

Physical Property	cement from spent shale
1. Fineness (cm^2/gm) (air permeability test, Blaine)	2230
2. Soundness (%) (autoclave expansion)	0.34
3. Consistency (%) (Vicat plunger)	26.60%
4. Setting Time (Vicat)	
Initial: minutes	98
Final : Hr : minutes	2:45
5. Air content of Mortar (%)	8.5
6. Compressive Strength (kg_f/cm^2)	
(i) 1 day in moist. air, 2 days in water	160
(ii) 1 day in moist. air, 6 days in water	216
(iii) 1 day in moist. air, 27days in water	294

Table 7.9 Comparison of the physical characteristics of commercial cements to cement from spent shale

Physical requirements	ASTM[2] (Portland cement Type I)	CEMENT FROM SPENT SHALE	ELEPHANT BRAND CEMENT	PAYANAK BRAND CEMENT
1. Fineness (cm^2/gm) Permeability Test, Blaine	ave. min. 2800 any one sample : ave. min. 2600	2230	ave. min. 3000 any one sample : ave. min. 2800	3737.5
2. Soundness (%) Autoclave expansion	max. 0.80	0.34	0.10	0.07
3. Normal consistency (%) Vicat Apparatus		26.6		
4. Time of Setting Vicat Apparatus				
initial, Min.	min. 45 minutes	98	125	133
Final , Hr:Min.	max. 10 hr	2:45		5:25
5. Air content of mortar (%)	max. 12	8.5	6.9	
6. Compressive strength (kg_f/cm^2) 1 day in moist air, 2 days in water	min. 85	160	150	167

Table 7.9 (Cont.)

Physical requirements	ASTM[2] (Portland cement Type I)	CEMENT FROM SPENT SHALE	ELEPHANT BRAND CEMENT	PAYANAK BRAND CEMENT
1 day in moist air, 6 days in water	min. 150	216	220	214
1 day in moist air, 27 days in water	min. 245	294	300	n.d.

All physical properties were within the ASTM standards except fineness. The fineness was too low.

From table 7.9 a comparison of the physical properties between cement from spent shale and Elephant brand cement reveals the following.

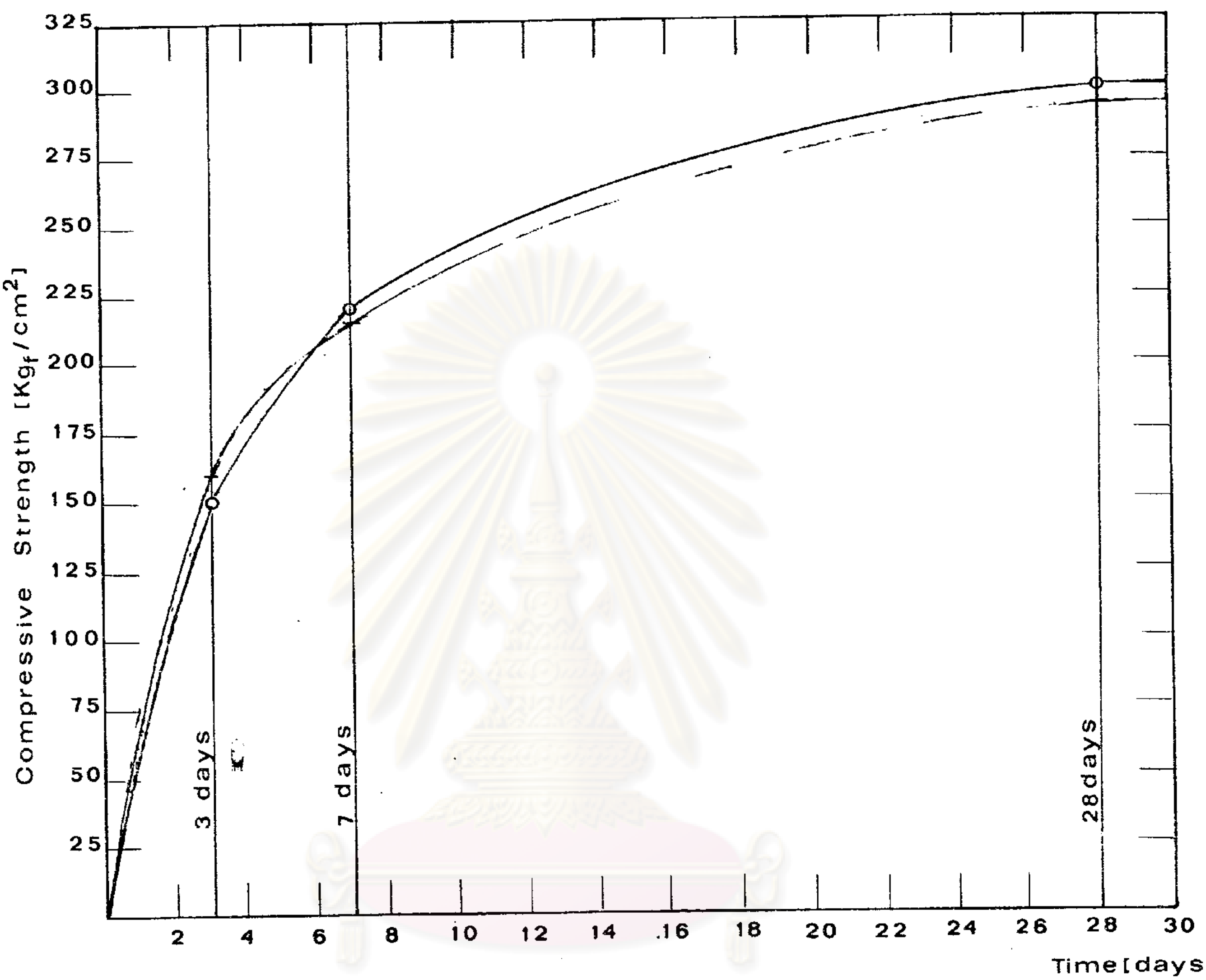
The percentage of autoclave expansion of cement from spent shale was higher than that of Elephant brand cement. If the maximum value of autoclave expansion is considered to equal 100%, Elephant brand cement measured 12.5% and cement from spent shale 42.5%. If the spent shale cement powder was ground more finely, the percentage dropped. Hence, the properties improved. Soundness indicates the workability of the cement under restraint. The expansion of free lime (CaO) and periclase (MgO) will cause unsoundness and disruption of the cement paste.

The setting time of cement from spent shale was too rapid in comparison with Elephant brand cement, but it still met ASTM standards, though the fineness was too low. If the cement powder was finer, the time of setting would be more rapid. Thus, the cement may be classified as a too-rapidly-hardening cement.

The air content of cement from spent shale mortar was 1.6 higher than Elephant brand cement. The packing of cement from spent shale was less dense than Elephant brand cement because of a lower degree of fineness causing more distribution of air in voids.

7.6 Compressive Strength

Figure 7.3 shows the compressive strength between cement from spent shale and Elephant brand cement. The early age strength of cement



—+— Cement From Spent Shale

—o— Elephant Brand Cement

FIGURE 7.3 COMPARISON OF COMPRESSIVE STRENGTH BETWEEN CEMENT FROM SPENT SHALE AND ELEPHANT BRAND CEMENT from spent shale slightly increased but then decreased at the later ages when compared with Elephant brand cement.

The broken cube specimens after the compressive test were subjected to x-ray diffraction. According to the diffracted patterns (Figure 7.4), the peaks found were as follows:

For CuKα radiation;

$$
\begin{aligned}
2\theta &= 18.00^{o} & d &= 4.92^{o}A \\
&= 29.30^{o} & &= 3.05^{o}A \\
&= 32.10^{o} & &= 2.78^{o}A \\
&= 32.40^{o} & &= 2.76^{o}A \\
&= 34.30^{o} & &= 2.61^{o}A
\end{aligned}
$$

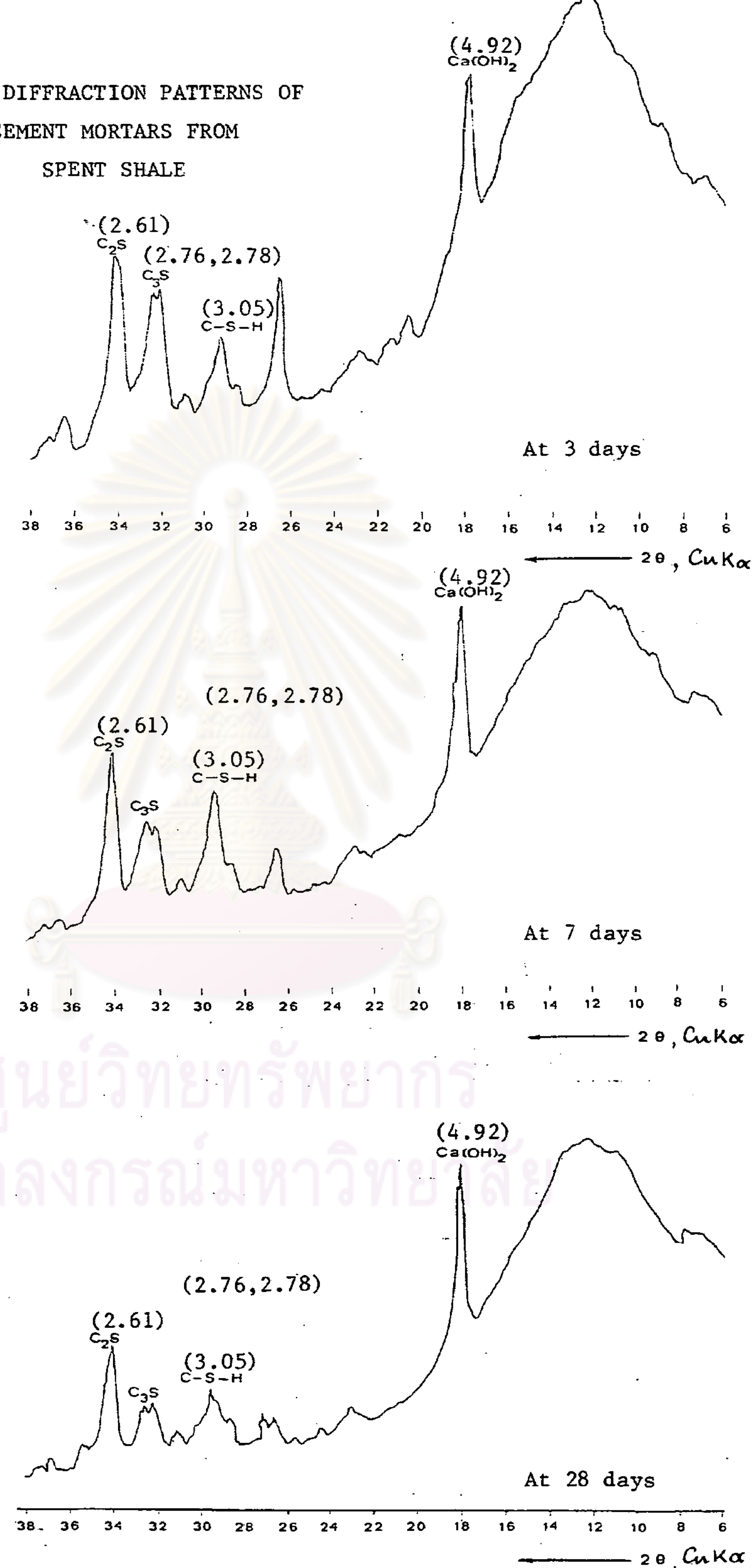
These are the same as in section 7.3 with the addition of $Ca(OH)_2$. Identification of the phase compositions is presented in table 7.10.

Table 7.10 Identification of the phase compositions

2θ	d (^{o}A)	Identified compound
18.00	4.92	$Ca\ (OH)_2$
29.30	3.05	C-S-H
32.10	2.78	C_3S
32.40	2.76	alite (C_3S)
34.30	2.61	β-C_2S

Using equation 6.2, the quantitative estimation of phases is shown in Table 7.11 and Figure 7.5.

Figure 7.4 X-RAY DIFFRACTION PATTERNS OF CEMENT MORTARS FROM SPENT SHALE



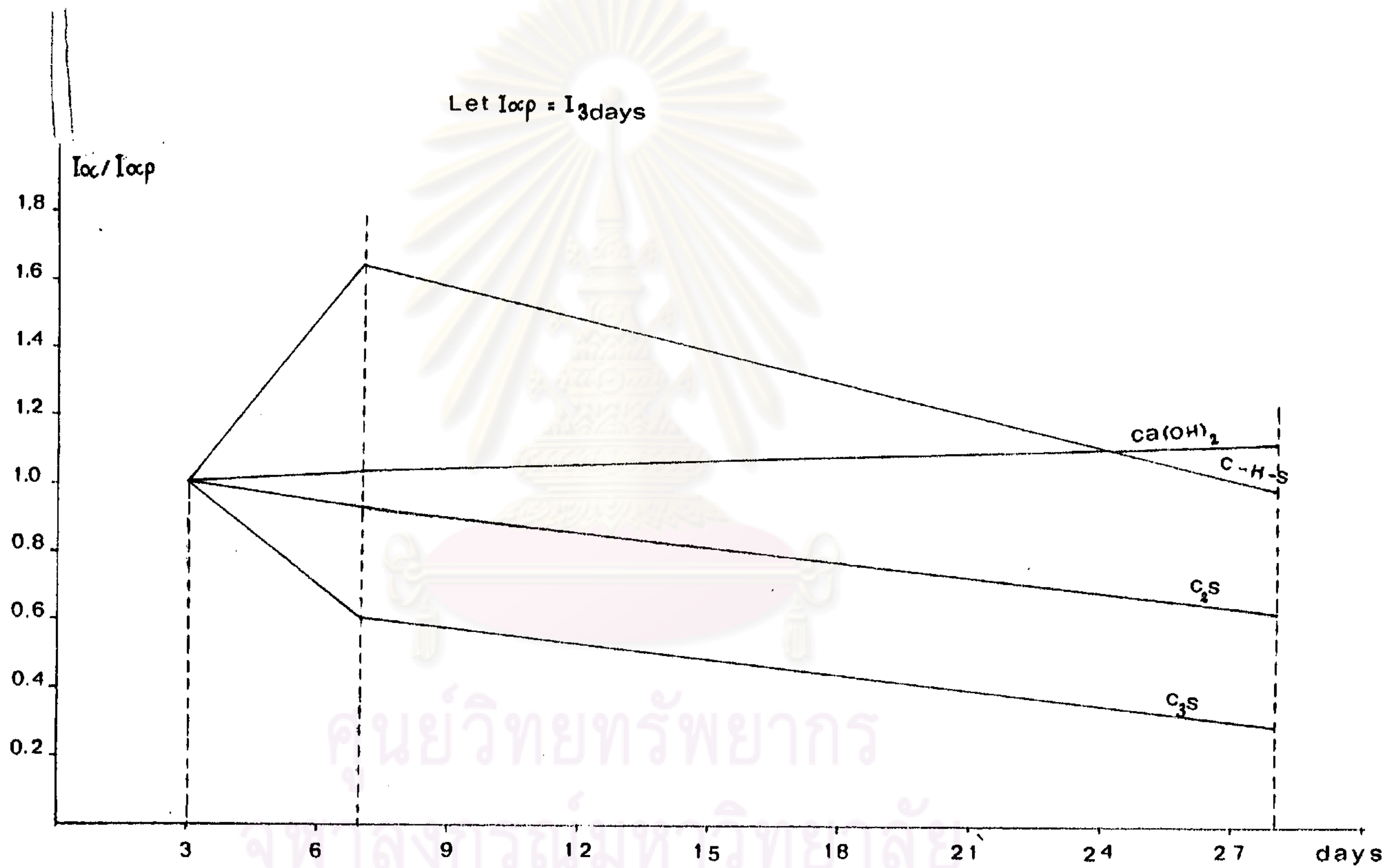


FIGURE 7.5 $I\alpha/I\alpha p$ of phase compositions of cement mortars from spent shale at various time with respect to $I\alpha/I\alpha p$ at 3 days

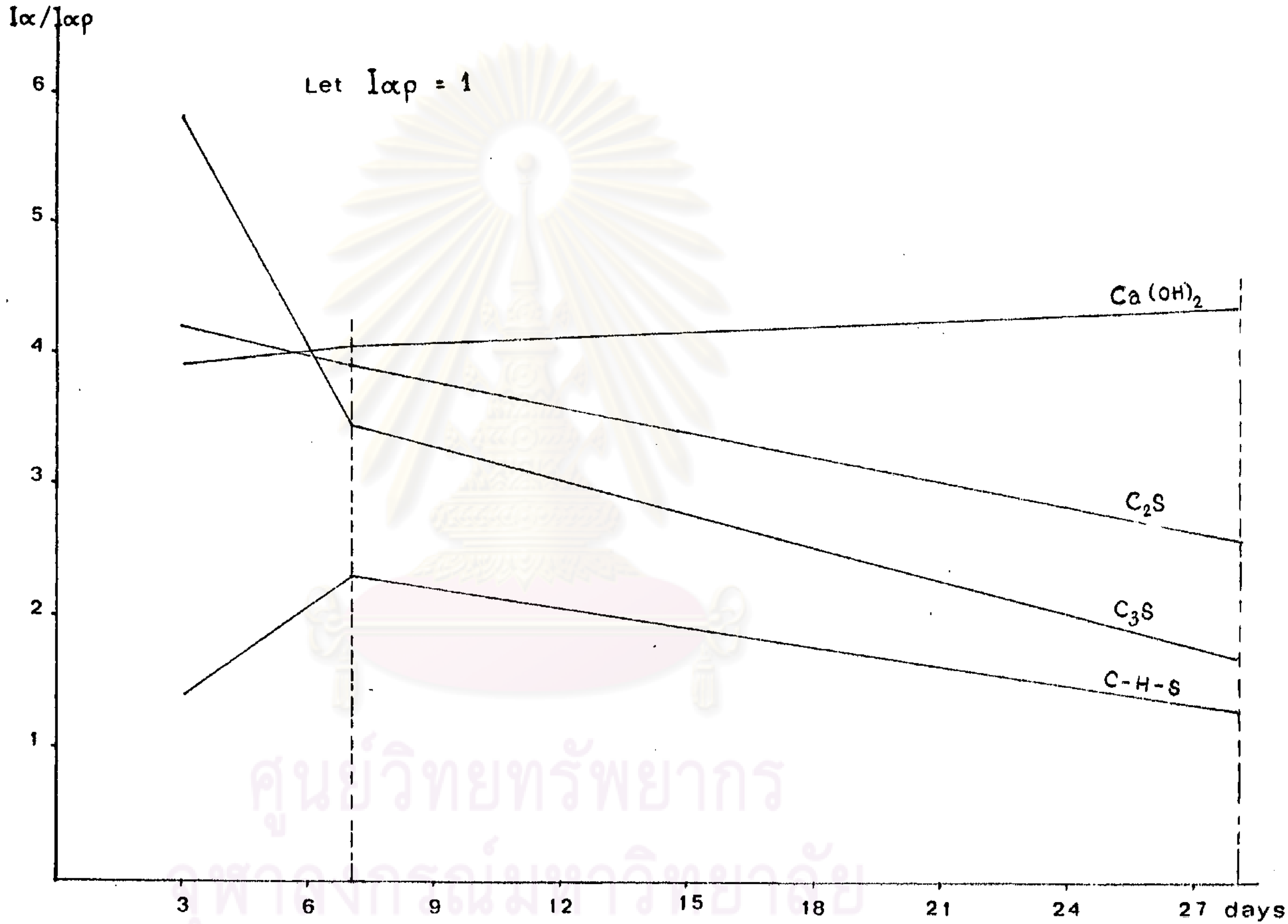


FIGURE 7.6 Iα/Iαp of phase compositions of cement mortars from spent shale at various time

Table 7.11 The quantitative estimation of cement mortar cubes phases at various ages

Age (days)	C_3S	C_2S	C-H-S	$Ca(OH)_2$
3	5.80	4.20	1.40	3.90
7	3.45	3.90	2.30	4.05
28	1.70	2.60	1.25	4.35
	Let Iαρ = Peak Intensity of strength at 3 days.			
3	1.00	1.00	1.00	1.00
7	0.60	0.93	1.64	1.04
28	0.29	0.62	0.89	1.12

The decreasing rate of C_3S in 7 days was steeper than at later ages (c.f. figure 7.5). This corresponded to the hydration reaction of C_3S.

As for C_2S, the rate steadily decreased. As long as hydration developed, the reaction of C_2S was slow at the early ages and faster after 7 days. Thus, the C_2S line in figure 7.5 should decrease rapidly at the later ages instead of gradually decreasing.

The $Ca(OH)_2$ continued to increase steadily corresponding to the rate of hydration.

The compound which did not react according to the theory was C-S-H which increased in 7 days, then decreased to less than the original amount at 3 days. But the theory[16] states that C-S-H may hydrolyze upon hydration, liberating some lime into the solution until the concentration is raised to the value required to stabilise it. Hence, the C-S-H line (figure 7.5) decreased at the later ages because it changed to other products or varied in the composition of the phases which resulted in displacement of lines in the x-ray spectra.