Chapter IV

Result

4.1 Appearance of Glass Melting

The appearance of 8 molten glass compositions were recorded at each step and samples were kept to compare the steps with each other. These results are shown in the following table.

Table 4.1 Appearance of glass melting.

Type	1st melt	2nd melt	3rd melt	fibres
JM1	-	-	bluish green seeds and small bubbles inside	$\phi \sim 156 \pm 56\ \mu m$, white, no spots, brittle
JM2	rather bluish green, no good melt	clear glass, bluish green, seeds	rather clear, bluish green	-

Type	1st melt	2nd melt	3rd melt	fibres
B4	black, no good melt. Still has stones, sharp crack	black, sharp crack, no spot or stones	black and luster at the surface	$\phi \sim 187 \pm 62$ μm, black and brown, brittle
B3	black, foam at the surface, still has stones, sharp crack	black, luster, sharp crack, no stones	black, brown	-
S1	soft green, stones	soft green, less stones	soft green, small bubbles inside, seeds	$\phi \sim 173 \pm 64$ μm, yellow green to white, some stones, seeds
S2	yellowish green, stones	yellowish green luster, sharp crack	yellowish green luster, small bubbles	-
E1	no good melt, big bubbles, a lot of foam on the surface white to green	less bubble and foam	cordy white to green, small bubbles inside	$\phi \sim 108 \pm 32$ μm, white, no stones, brittle

Type	1st melt	2nd melt	3rd melt	fibres
E 2	the same as E 1	less bubble and foam	small bubble and seeds inside	-

4.2 Density Determination

In order to present the corrosion rate of glass, density is a key property which was required. Results are show in the following table.

Table 4.2 Density of 8 glass compositions.

Table 4.2 Density determination

Sample	D(g/cm3)	S.D.
JM1	2.512	0.002
JM2	2.537	0.001
B3	2.824	0.002
B4	2.831	0.003
S1	2.847	0.002
S2	2.843	0.002
E1	2.593	0.001
E2	2.587	0.001
Std gl.	2.487	0.004

From the above table, these glasses have the density in the range of 2.49 - 2.85 g/cm^3 and their standard deviation (N - 1) was in the range of 0.001 - 0.004. Both JM and E glass had densities smaller than basalt and slag glass.

4.3 Chemical Analysis

Table 4.3a Chemical analysis from EDX (3 standard samples)

	SiO2	TiO2	Al2O3	Fe2O3	MgO	CaO	Na2O	K2O
DGG	72.33	0.12	1.10,	0.12	4.55	6.74	15.23	0.33
SON-68	43.86	-.-	5.09	3.06	-.-	4.15	9.35	0.04
GH-4	45.70	2.69	12.94	12.26	9.25	10.74	3.15	1.37
DGG *	71.72	0.19	1.23	0.14	4.18	6.73	14.95	0.38
SON-68 *	45.50	-.-	4.90	2.90	-.-	4.00	9.90	-.-
GH-4 *	45.10	2.69	13.00	12.30	9.43	10.80	2.88	1.36
JM1	61.13	-.-	4.20	0.16	0.32	4.85	6.68	1.51
JM2	65.91	-.-	6.10	0.26	-.-	10.02	5.54	2.86
B4	49.62	2.56	13.28	11.04	-.-	16.15	0.66	3.25
B3	39.14	2.75	10.84	9.97	4.87	9.94	0.70	1.92
S1	40.68	-.-	15.56	0.11	1.61	26.32	0.93	1.48
S2	46.68	-.-	19.01	0.11	-.-	29.87	1.94	1.53
E1	55.71	-.-	15.75	0.15	1.02	16.35	1.07	0.04
E2	58.45	-.-	16.70	0.14	-.-	20.00	1.19	-.-

* = standard composition

Table 4.3b Chemical analysis from EDX (5 standard samples)

	SiO2	TiO2	Al2O3	Fe2O3	MgO	CaO	Na2O	K2O
DGG	71.77	0.15	1.24	0.19	3.95	6.76	14.96	0.39
SON-68	48.26	0.07	4.63	2.93	0.33	4.22	10.26	0.02
ESCA (A)	46.16	-.-	4.86	4.58	-.-	4.11	9.97	-.-
ESCA (B)	47.99	0.06	5.32	11.93	0.21	4.56	9.61	0.03
GH-4	45.44	2.68	12.98	12.29	9.50	10.78	2.92	1.36
DGG *	71.72	0.19	1.23	0.14	4.18	6.73	14.95	0.38
SON-68 *	45.50	-.-	4.90	2.90	-.-	4.00	9.90	-.-
ESCA (A)*	45.30	-.-	4.90	-.-	-.-	4.40	9.90	-.-
ESCA (B)*	51.70	-.-	5.00	-.-	-.-	4.50	10.10	-.-
GH-4 *	45.10	2.69	13.00	12.30	9.43	10.80	2.88	1.36
B4	47.44	3.63	14.82	11.16	12.53	16.14	2.28	2.58
B3	40.59	2.34	11.62	9.89	7.59	9.98	4.08	1.37
E1	51.23	2.84	16.66	0.74	13.37	16.35	0.47	1.78
E2	52.96	3.56	18.15	0.80	16.33	19.97	-.-	2.25
S1	40.37	4.69	18.71	0.53	23.68	26.23	0.35	3.48
S2	43.98	5.52	21.92	0.76	26.38	29.76	-.-	4.01
JM1	60.23	0.05	4.54	0.25	1.13	4.91	10.81	0.49
JM2	62.79	1.07	7.28	0.50	5.88	10.04	9.16	1.56

* = standard composition

From the above table, chemical analysis from EDX indicates changes of 0.5-8% Even though 5 and 3 samples cps standard method was used. These may rather not come from the melting process. The main cause may came from the fact that this thesis work was the last group to analyze before the equipment was broken, and shut down for 2 months.

So, the nominal chemical compositions were selected to calculate dissolution Gibbs free energies.

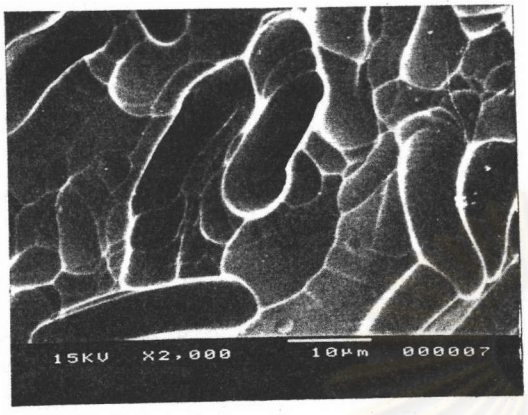
4.4 Morphology of the Glass Surface After Corrosion Tests

Both chips and fibres were analyzed by SEM. The following figure shows El glass tested under 3 different conditions.

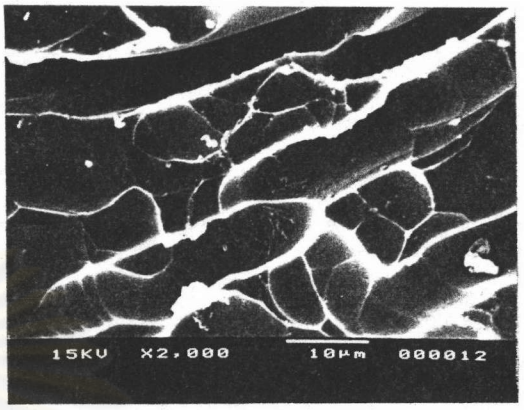
Fig. 4.1 SEM morphology of E glasses; a) Gamble's solution saturated with N_2, 28 days, b) Gamble's saturated with N_2, 56 days, c) none, d) buffer solution at pH 5, 56 days.

From the above figure, at pH 5, El glass was more stable. A deep line defect (skratch) which may come from cutting is still there even after corrosion.

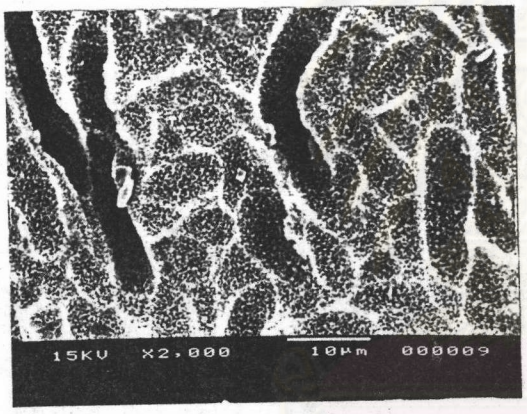
The other samples are shown in the figures below. When glass had dissolved much sharp surface edges had gone (such as with the buffer solution at pH 5, 56 days).



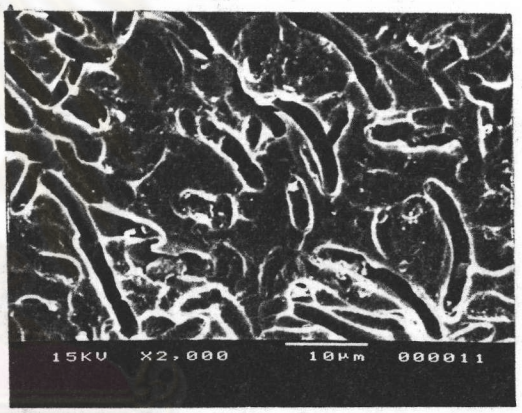
a



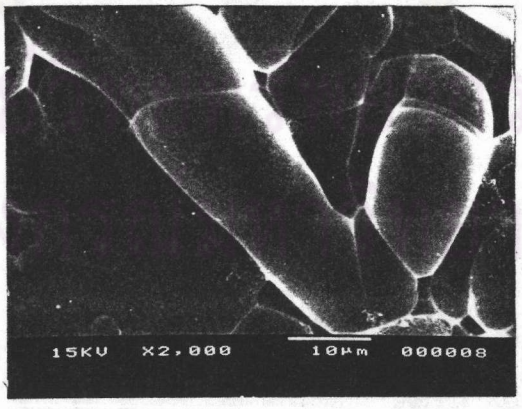
b



c



d

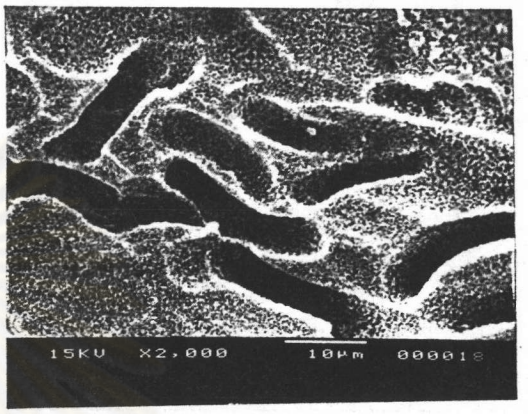


e

Fig. 4.2 SEM morphology of basalt JM and slag; a) B4-56 days (PO_4^{2-}) b) B4-56 days (pH5), c) B3-56 days (PO_4^{2-}), d) JM1-56 days (pH5), e) S1-56 days (N_2)

The last group of SEM images shows samples with binder (B3 and S2) which were corroded by Gamble's solution for 42 days. After corrosion, the binder was almost gone.

a



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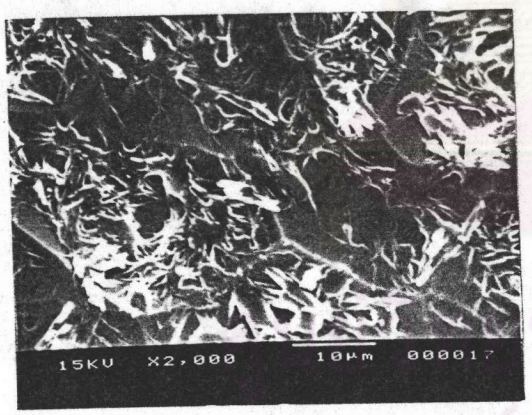

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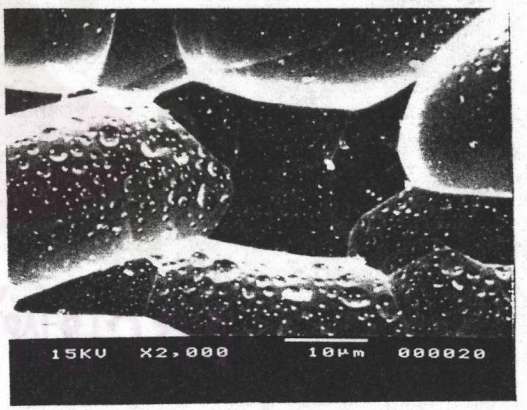
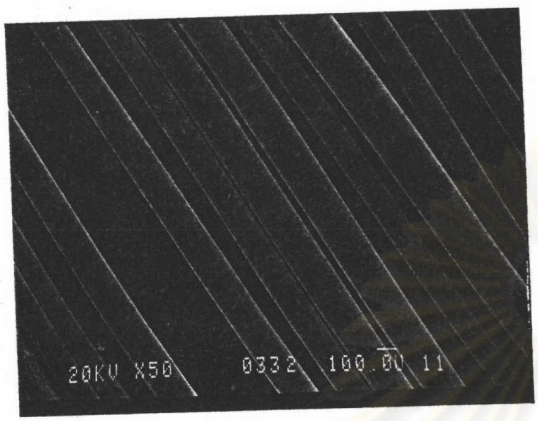


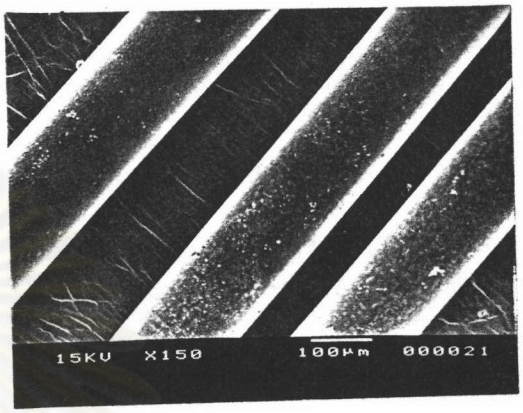
d

Fig. 4.3 SEM morphology of basalt and salg coated with binder; a) B3 (un-corroded), b) B3 corroded in Gamble's solution, 42 days, c) S2 (un-corroded) and d) S2 corroded in Gamble's solution, 42 days.

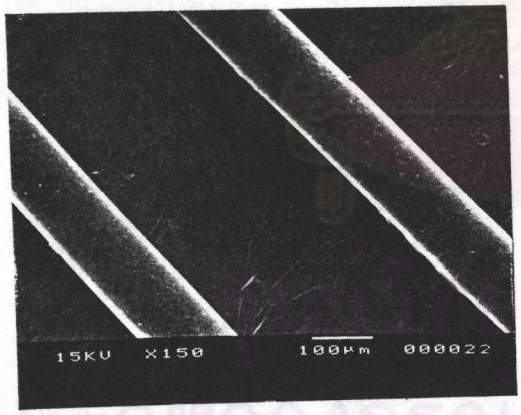
For fibre samples, a change of the fibre surface before and after corrosion can hardly be detected by SEM as shown in the figures below.



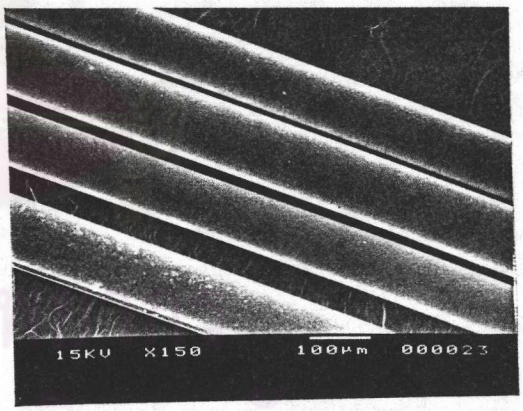
a



b



c



d

Fig. 4.4 SEM morphology of basalts and slag fibres; a) B4-(un-treated), b) B4-N_2 (7 days), c) E1-(untreated), d) E1-N_2 (7 days)

4.5 Corrosion Rate of Chip and Fibre Samples

4.5.1 Gamble's Solution Test

8 glass compositions and 4 times interval were done. Some groups were tested for 112 days. These results was shown in the figure and table below. In the following, the group JM1, B4, S1 and E1 will be called glass 'group one' which had high MgO content and JM2, B3, S2 and E2 will be called glass 'group two' which had lower MgO but higher CaO content.

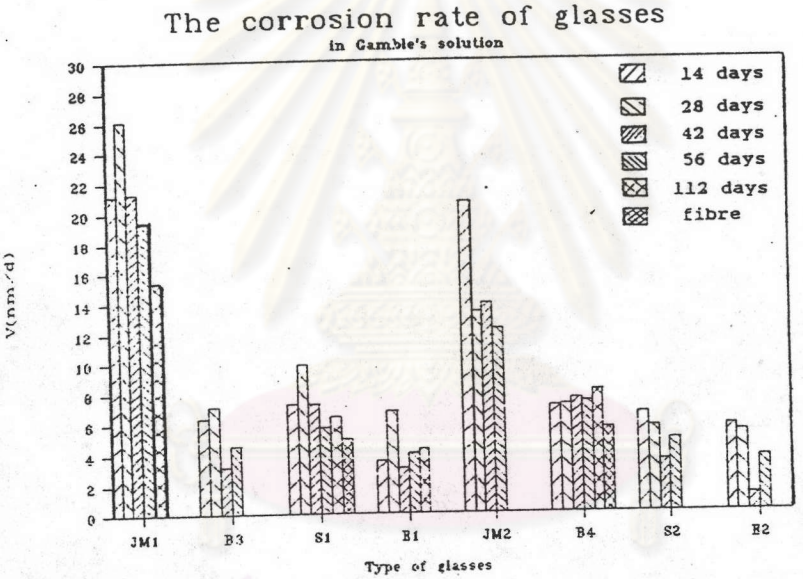


Fig. 4.5 Dissolution rate of glasses in Gamble's solution

Table 4.4 Glass dissolved in Gamble's solution

Type	V(nm/d)						fibre
	14	28	42	56	112	avg	7
JM1	21.15	26.11	21.34	19.39	15.40	22.28	-.-
B3	6.37	7.15	3.14	4.54	-.-	4.94	-.-
S1	7.25	9.90	7.25	5.74	6.43	7.63	4.96
E1	3.52	6.74	2.98	3.99	4.30	4.57	-.-
JM2	20.61	13.33	13.91	12.18	-.-	13.14	-.-
B4	7.04	7.12	7.58	7.33	8.12	7.34	5.59
S2	6.56	5.68	3.46	4.80	-.-	4.65	-.-
E2	5.71	5.35	1.13	3.62	-.-	3.36	-.-

From the above figure, the corrosion rate of these glasses can be classified into 3 types. The first type was JM glass which had a dissolution velocity in the range of 15-21 nm/d for JM1 and 12-21 nm/d for JM2 glass. The second type was basalt and slag glasses. They had a corrosion rate in the range of 4-9 nm/d. The third type is E glass; the corrosion rate was in the range of 3-6 nm/d. The results also showed that except for basalt, glass group one had a corrosion rate higher than group two of approximately 36% for JM glass, 37% for slags and 25% for E glass. This may be summarized as an overall 30% effect. When the factor of time is considered, the JM glassed have high initial rates, slowing down with time. The other glasses scatter around an average rate right from the beginning.

The effect of geometry on the corrosion rate of glass was determined by using fibre samples. The results show that fibres had corrosion rates lower by approximately 26% for B4, and 32% for S1 For E glass, the effect could not be manifested due to the scatter of the chip data.

4.5.2 Gamble's Solution Saturated With N_2

The results for this condition seem to follow the classification in three types again. These are 15-24 nm/d for JM glass, 7-11 nm/d for basalts and slag glasses and 5-7 nm/d for E glass as shown in the figure and table below.

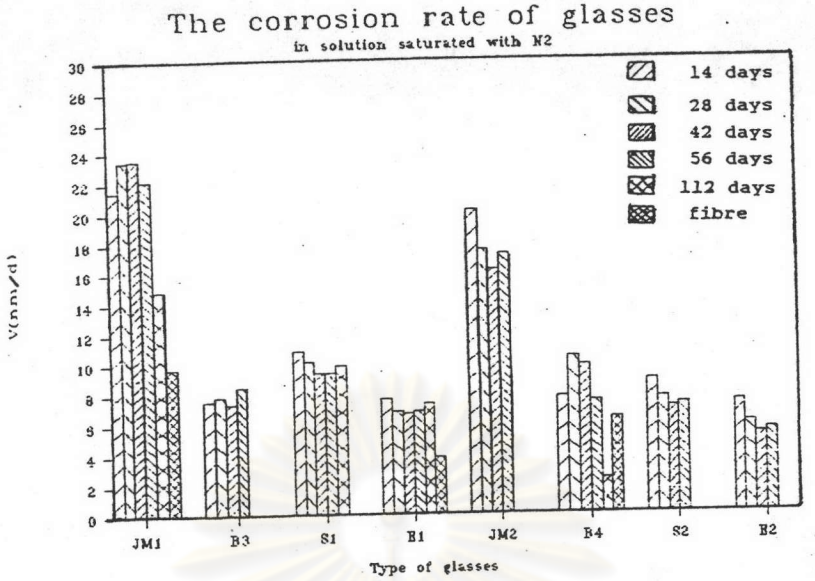


Fig. 4.6 Dissolution rate of glasses in Gamble's saturated with N_2

Table 4.5 Glass dissolved in Gamble's solution saturated with N2

Type	V(nm/d) 14	28	42	56	112	avg	fibre 7
JM1	21.46	23.46	23.55	22.13	14.82	23.04	9.72
B3	7.56	7.79	7.35	8.41	-.-	7.85	-.-
S1	10.83	10.11	9.37	9.33	9.85	9.60	-.-
E1	7.63	6.79	6.60	6.80	7.29	6.73	3.69
JM2	20.05	17.41	16.13	17.15	-.-	16.90	-.-
B4	7.71	10.31	9.77	7.39	2.27	9.16	6.26
S2	8.80	7.61	7.02	7.16	-.-	7.26	-.-
E2	7.29	5.94	5.22	5.46	-.-	5.54	-.-

From the above figure, the corrosion rate of glass group one was higher than that of group two by approximately 19% for JM glass, 25% for slag, 19% for E glass and 5% for basalt. The corrosion rate of all glasses seem to be constant at long time corrosion and the geometry effect was lower as much as 52% for JM glass, 16% for slag and 46% for E glass.

When comparing results of N_2 saturated solution to those of Gamble's solution, and increase was found.

4.5.3 Gamble's Solution with no Phosphate

The results can be separated into 3 types; JM glass, slag glass and basalt and E glass which have a corrosion rate in a range of 12-25 nm/d, 2-9 nm/d and 1-4 nm/d respectively. As to the fibres, they had a large difference from chip samples for JM amd basalt. For E glass, the result is uncertain.

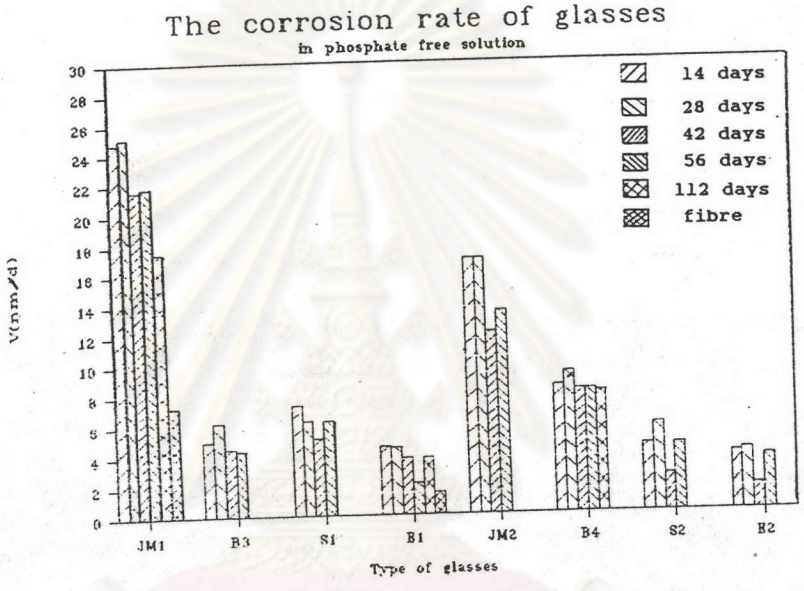


Fig. 4.7 Dissolution rate of glasses in phosphate free solution.

Table 4.6 Glass dissolved in Gamble's solution with no phosphate

Type	V(nm/d) 14	28	42	56	112	avg	fibre 7
JM1	24.82	25.13	21.63	21.83	17.50	22.86	7.27
B3	4.96	6.24	4.45	4.33	-.-	5.00	-.-
S1	7.32	6.30	5.13	6.27	-.-	5.90	-.-
E1	4.56	4.50	3.77	2.14	3.76	3.47	1.47
JM2	16.95	16.91	12.04	13.46	-.-	14.14	-.-
B4	8.43	9.35	8.17	8.14	8.05	8.55	3.39
S2	4.47	5.90	2.43	4.51	-.-	4.28	-.-
E2	3.86	4.04	1.71	3.62	-.-	3.12	-.-

4.5.4 Samples Coated Binder in Gamble's Solution

The samples coated with commercial binder showed an effect up on corrosion. An enhanced corrosion rate was found with approx. 23% for JM2, 9-10% for B3, S2 and E glasses which had more CaO content. A retarding one was found with JM1, S1 and E1 glasses approx. 26% for JM1 and 5% for S1 and E1 glasses. These results are shown in the following figure and table.

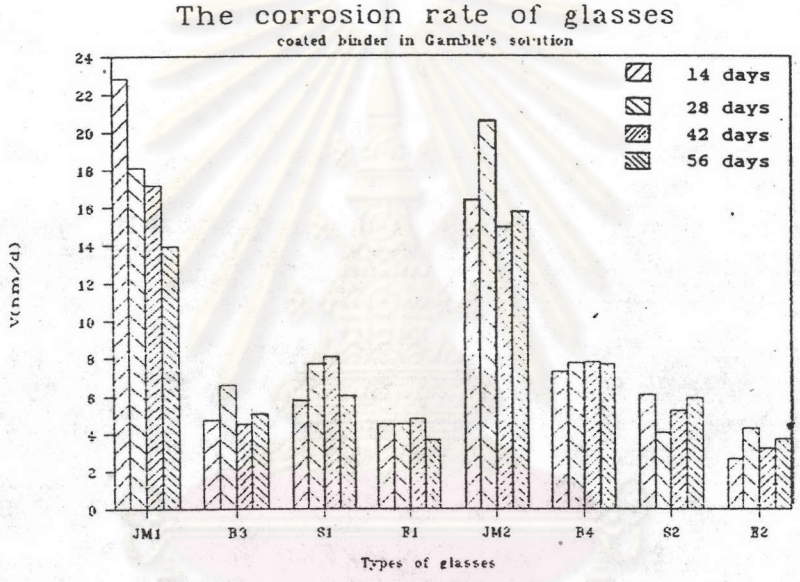


Fig. 4.8 Dissolution rate of glasses in Gamble's solution with sample coated and not coated binder.

Table 4.7 Glass dissolved in Gamble's solution with sample coated with binder

Type	V(nm/d)				
	14	28	42	56	avg
JM1	22.87	18.14	17.18	13.93	16.41
B3	4.75	6.60	4.54	5.11	5.42
S1	5.74	7.72	8.11	6.01	7.28
E1	4.52	4.52	4.79	3.67	4.33
JM2	16.41	20.62	14.92	15.76	17.10
B4	7.33	7.74	7.81	7.69	7.75
S2	6.09	4.07	5.26	5.95	5.09
E2	2.68	4.28	3.27	3.72	3.76

4.5.5 Buffer Solution at pH 5

At pH 5, totally different corrosion rate of glasses were obtained. These results are shown in the figure and table below.

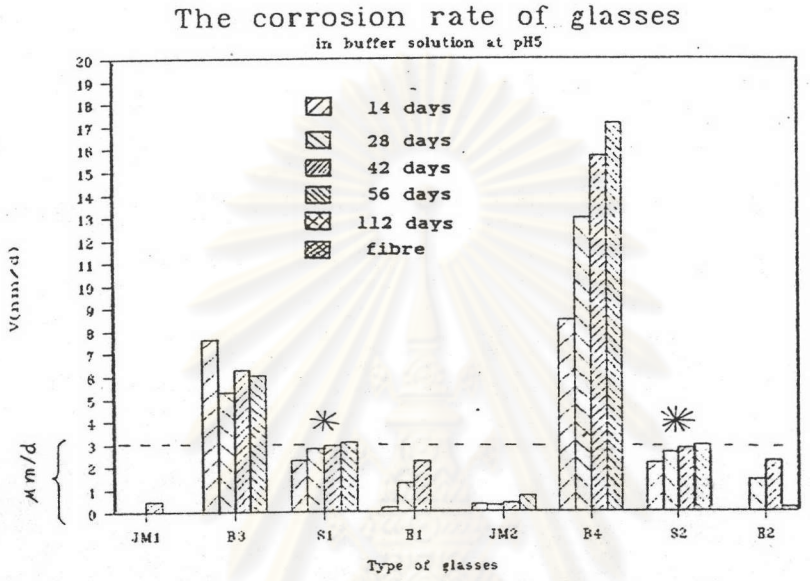


Fig. 4.9 Dissolution rate of glasses in buffer solution at pH 5, for glasses S1, S2, the alternative µm /d scale is valid

Table 4.8 Glass dissolved in buffer solution at pH 5

Type	V(nm/d)					fibre
	14	28	42	56	avg	7
JM1	-.-	-.-	0.47	-.-	0.47	-.-
B3	7.64	5.32	6.29	6.04	5.88	-.-
S1	2303.93	2782.44	2957.62	3068.46	2936.17	-.-
E1	0.21	1.26	2.25	-.-	1.76	-.-
JM2	0.37	0.30	0.39	0.69	0.46	-.-
B4	8.44	12.96	15.69	17.12	15.26	1.91
S2	2172.31	2595.64	2825.21	2931.24	2784.03	-.-
E2	-.-	1.40	2.26	0.20	1.29	-.-

From the above figure, JM and E glass had corrosion rates of 0.2-2.3 nm/d, but basalts and slags had a dissolution rate in the range of 24-51 nm/d for B4, 15-21 nm/d for B3 and in the range of 2000 nm/d for slag glasses.