Research Paper 10

A Study of Pore Size Distributions in Fired Clay Bricks in Relation to Salt Attack Resistance

Abstract

The pore size distribution of fired clay bodies formed by extrusion was studied with the aid of a mercury porosimeter. The results of these investigations were then related to the criterion postulated by Zsembery and Phillips[3] for grading fired clay bodies according to their resistance to cycles of soaking in a sodium sulphate solution followed by oven drying. The same 55 samples of 11 Victorian clay mixtures prepared and fired by Zsembery and Phillips were used again in these investigations.

Over the range of temperatures studied, total porosity decreased from around 30 percent on firing at 900°C to around 20 percent at 1100°C.

Until the fusion point of a particular body was reached, this decrease in porosity with increased firing temperature was accompanied by a significant increase in the diameters of the modal pore sizes contained in the body. As more of the body fuses, the larger pores seal over so that total open porosity is reduced.

Pore size distribution does not itself provide an adequate guide for grading these bodies into order of their resistance to soluble salt attack. The relationship between salt attack resistance, as measured by the salt cycling method, and total porosity or Rockwell hardness seems to be better than that between salt attack and pore size distribution. It is possible that rapid tests of hardness and porosity could broadly differentiate bricks of both poor and good durability classes, and minimize long term testing. Near cut-off boundaries, results from these fast methods would give ambiguous results. However, further work is needed before any of these techniques may be used with confidence to predict brick durability.

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A Study of Pore Size Distributions in Fired Clay Bricks in Relation to Salt Attack Resistance

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From: Proceedings of the Seventh International Brick Masonry Conference, Melbourne, February 1985

ISBN 0 947 160 12 4

First published 1985, published in PDF (Acrobat) format May 2002

Editor's note: The image quality of some figures reflects that of the best available source material.

1.0 Introduction

The porosities and pore size distributions of fired clay bricks have been considered to be important factors in determining resistance to salt attack, resistance to frost and strength. It was reported by A. Watson, J.O. May and B. Butterworth[1] that more frost resistant bricks had a smaller volume of fine pores than the less frost resistant.

Working on various brick clays, R.D.Hill[2] showed that the higher the firing temperature, the greater tendency for a coarse pore structure to develop. The present report attempts to correlate the pore size distributions of sets of extruded bars of single clays and brick bodies fired at different temperatures and their salt cycling resistance as measured by D.N. Phillips & S.Zsembery[3].

2.0 Raw materials

Raw materials and production blends provided by two Victorian clay brick manufacturers were used as follows:

1. Enfield Yellow (YE)
2. Pit Shale (PS)
3. Enfield Grey (GE)
4. Bacchus Marsh Clay (BM)
5. Light Reef Clay (LCR)
6. Wollert Plastic Clay (WP)
7. Cream Brick Mix 1 (C)
8. Red Brick Mix (R)
9. Brown Brick Mix (BR)
10. Cream Brick Mix 2 (CR)
11. Pink Brick Mix (P)

C = 30% CW + 65% GE + basalt

R = 48% PS + 47% YE + basalt

BR = 48% PS + 47% YE + Mn02

CR = 50% BM + 40% LCR + 10% other

P = 20% WP + 20% LCR + 60% other

3.0 Experimental

The test pieces were fired at temperatures ranging from 900 to 1100°C in a programmed Tetlow kiln adopting a 5 hour heating period, a 5 hour soak period and subsequent cooling to ambient temperature over a total 24 hour cycle. Temperatures were monitored with No.27 Buller rings.

Pore size distributions of the test pieces were determined by mercury intrusion porosimetry. The apparatus used was a Carlo Erba mercury porosimeter which measured the distributions of pores with radii between 75,000 and 37 A (corresponding to pressures ranging from 0.0098 MPa to 9.8 MPa). Checks on total pore volume were made by the evacuation method (BS 784:1973). The total pore volumes usually agreed with the results obtained from the mercury porosimeter within 0.5 percent.

4.0 Results

The original data were in the form of cumulative pore volumes into which mercury was forced by progressively increasing pressure. This was recalculated by interpolating the volumes filled at mercury pressures that would enter pores with the following diameters (actually neck diameters): 10, 1.6, 0.8, 0.04, 0.2, 0.08 and 0.04 microns. Pore size distributions in eight size ranges bounded by these diameter values are given in Table 1 and the results for representative brick mixes (C,R and P) are presented as histograms in Figures 1, 2 and 3. Table 1 also gives the results of salt cycling tests and hardness measurements on all bodies at the five temperatures.

Histograms showing the frequency of various pore size parameters and their relation to hardness and durability to salt cycling (after Phillips and Zsembery) are given in Figure 4. Figure 5 shows the relationship between salt durability, hardness, total porosity and various groupings of pore sizes.

An examination of the pore size distributions of most clays and brick bodies in Table 1 shows them to be predominantly unimodal with the modal values chiefly in the ranges 1.6 to 0.08 microns.

Some bodies show a slight departure from unimodality by having a small secondary peak in the 0.04 - 0.015 micron range. The one unique clay is WP which is distinctly bimodal, with peaks at the coarse and fine pore sizes. The clay has the highest volume of fine (0.04 – 0.015 microns) pores of all bodies (at 900°C) and the highest volume of coarse (10-1.6 microns) pores of all bodies at 1050 and 1100°C. It has the highest resistance to salt attack of all the bodies at the 900°C firing and the least resistance at the 1100°C firing.

With increasing firing temperature the finer pores are eliminated (or become sealed pores) and the modal pore value shifts to larger pore diameter ranges. Thus, as shown in Figure 4, the modal pore value is 0.4 - 0.2 microns at 900°C, 0.8 - 0.4 microns at 960 and 1000 OC, and 1.6 - 0.8 microns at 1050 and 1100°C. Large pores (over 1.6 microns) develop noticeably at the 1100°C firing. The same trend to pore coarseness can be seen from the histograms of the two most frequent pore size ranges (Figure 4). Coarsening of pore sizes with increasing temperature is accompanied by a reduction in total porosity, as also portrayed in Figure 4.

Microscopic examination of similar bodies and comparison with other ceramic investigations of sintering suggest that closing of finer pores as firing proceeds is due to sealing of pores by surface tension effects in liquid body components, by migration of pores along grain boundaries and by coalescence of smaller pores into larger ones. Larger pores are produced mostly by shrinkage effects causing star cracking around more refractory particles and by pull apart on laminar structures to accommodate differential shrinkage.

Overall shrinkage of the body, especially at 1050 and 1100°C, reduces total porosity. The effect is accentuated by manganese dioxide which promotes melting (see BR results, 1050 and 1100°C Table 1).

In Figure 5, a plot of hardness against total porosity shows a sigmoidal alignment of bodies. Low durability bodies are found at the low hardness, high porosity end of the band and high durability ones at the high hardness, low porosity end. The dotted lines define areas for these bodies which correspond to the salt durability at the transition from intermediate to high durability categories of Phillips and Zsembery, i.e. high durability (over 40 cycles of 14 percent w/v sodium sulphate decahydrate crystallisation), intermediate durability (10 - 40 cycles) and poor durability (less than 10 cycles). Relatively small increases in hardness or reduction in porosity are accompanied by large increases in durability from 20 - 30 to over 80 cycles. In these bodies a significant degree of glass formation occurs at this transition. The zone of intermediate durability show anomalous relationships of durability to hardness and porosity.

Specimens with high resistance to salt attack were those fired at 1100°C. These were characterised by high hardness (greater than 95), reduced total porosity (less than 20 percent), and a diminution in the percentage of fine pores (less than 6 percent porosity in pores 0.2 microns diameter and smaller).

Specimen with poor resistance to salt attack (i.e. failure in 10 cycles or less) were those fired at 900, 960 and 1000°C. They were characterised by hardness less than 60, total porosity 25 percent or greater, and usually more than 5 percent porosity in pores 0.2 microns diameter and smaller.

Specimens of intermediate salt resistance (failure in 10 to 40 cycles) were fired at 1000 and 1050°C, had hardness of 60 to 95, and total porosities in the range 30 to 20 percent.

Figures 5B, C and D give the relationship of different parts of the pore volume to hardness and durability. Figure 5B shows the reduction in fine pores that accompanies the trend to higher temperatures and durability. Figure 5D shows that large pores account for a very small fraction of the pore volume of low and intermediate durability bodies, but increase somewhat for high durability and temperature. It is clear however from Figure 5A and C that the bulk of the pore volume occurs in two or three subdivisions of intermediate diameter and it is very likely that the disruptive effects of salt crystallisation are exerted most effectively on these middle size pores largely because they are the most numerous. The attitude of the boundary between zones of different durability in Figures 5B, C and D suggest that durability is more sensitive to hardness variation than to porosity in all ranges of diameter.

5.0 Discussion

Durability of clay bodies against salt attack clearly results from the balance between disruptive forces exerted in the walls of open pores and the strength of the body (quantified by hardness in this investigation). The fewer the open pores the less effective is the force exerted per unit volume, hence the lower the porosity the greater the durability. The same volume porosity would represent many more small pores than pores of intermediate or large diameter, so elimination of fine pores in the course of firing would have a reinforcing effect on improving durability to salt crystallisation.

Hardening, which increases progressively with increase in firing temperature, and is due to recrystallisation and cross bonding by the glassy phase, plays a very significant if not preponderant role in resisting salt attack.

Tests of hardness and porosity can be carried out much more rapidly than salt cycling to failure. By using correlations of these properties with durability for a wide spectrum of brick types, reliable estimates of durability can be offered to brick users without the need for protracted salt cycling or exposure testing.

6.0 Acknowledgements

The authors wish to thank Dr. W.F. Cole and Mr. P. Westgate of CSIRO (Division of Building Research, Highett) for their most helpful assistance in the mercury porosimetry work and for providing laboratory facilities. Thanks are also due to Mr. J. Vucko for his able assistance during this project. Financial assistance from Brick Development Research Institute to the first author is gratefully acknowledged.

7.0 References

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Table 1. Relation between salt cycles to failure, hardness, total porosity and pore size distribution

Sample	Na_2SO cycles	Hardness	Total % porosity	% porosity of various size pores (microns)							
				>10	10-1.6	1.6-0.8	0.8-0.4	0.4-0.2	0.2-0.08	0.08-0.04	0.04-0.015
900ºC											
YE	7	45	30.95	0.14	0.23	0.02	4.76	10.70	.6.06	3.98	5.04
PS	6	31	34.34	0.18	0.30	15.75	9.70	3.71	2.45	1.01	1.25
GE	7	37	28.41	0.13	0.21	0.02	0.01	0.60	16.03	5.97	5.44
BM	4	12	37.97	0.62	1.04	0.10	2.81	20.47	8.29	2.61	2.04
LCR	5	14	36.08	0.55	0.92	0.09	10.65	11.09	7.89	2.34	2.56
W	11	53	29.40	1.92	4.22	5.92	1.72	0.84	2.83	1.67	10.27
C	8	29	30.20	0.29	0.49	0.05	2.46	13.96	6.33	3.56	3.06
R	8	39	31.11	0.34	0.57	0.98	12.76	5.98	4.82	2.90	2.76
BR	9	47	29.19	0.14	0.24	0.02	12.64	5.89	4.88	2.84	2.54
CR	5	20	34.81	0.61	1.02	0.10	1.79	17.21	8.69	3.01	2.38
P	7	37	31.72	0.04	0.07	0.01	11.59	7.30	7.52	3.59	1.59
960ºC											
YE	9	60	29.36	0.26	0.44	0.26	13.11	6.79	4.33	1.19	2.97
PS	7	57	31.79	0.44	0.74	19.25	7.54	2.26	0.79	0.22	0.55
GE	9	57	26.35	0.39	0.66	0.06	0.03	11.06	9.66	3.06	1.42
BM	S	22	37.95	0.25	0.42	0.04	15.06	14.04	5.09	1.66	1.39
LCR	6	30	34.56	0.19	0.33	0.30	19.81	8.63	3.67	0.70	1.20
WP	14	54	28.65	0.17	12.36	3.85	1.92	1.25	1.84	2.58	4.69
C	10	59	27.62	0.20	0.34	0.06	13.40	7.84	3.87	1.19	0.71
R	9	65	27.41	0.34	0.58	6.95	12.35	4.05	2.18	0.42	0.53
BR	13	73	26.36	0.22	0.37	9.94	9.61	3.44	1.94	0.58	0.27
CR	7	33	34.11	0.15	0.26	0.02	14.21	11.74	5.29	1.07	1.36
P	10	56	29.21	0.15	0.25	5.93	11.43	6.33	3.51	1.05	0.57
IOOOºC											
YE	12	74	28.15	0.15	0.25	0.69	17.29	5.65	2.99	0.71	0.51
PS	10	62	29.48	0.15	3.61	19.27	4.44	1.03	0.40	0.06	0.53
GE	12	76	23.72	0.22	0.37	0.03	0.02	13.66	7.30	1.29	0.84
BM	6	28	36.74	0.38	0.64	0.06	19.15	10.28	4.01	0.89	1.32
LCR	8	43	32.90	1.59	2.67	2.32	18.23	4.96	1.81	0.21	1.12
WP	15	55	27.67	0.31	12.67	3.56	1.70	1.35	2.28	2.57	3.24
C	13	72	26.28	0.21	0.36	0.03	16.26	5.92	2.52	0.65	0.33
R	12	73	25.56	0.34	0.98	13.81	6.68	2.20	1.00	0.26	0.29
BR	14	82	23.38	0.13	0.57	10.41	8.13	2.45	1.13	0.15	0.40
CR	10	40	33.08	0.15	0.25	0.02	19.94	7.99	3.21	0.47	1.03
P	16	64	28.33	0.11	0.19	6.13	12.70	5.84	2.47	0.56	0.32
1050ºC											
YE	22	82	24.65	0.14	0.24	9.52	9.92	3.08	1.13	0.38	0.24
PS	19	77	24.32	0.10	10.18	11.18	11.13	1.81	0.49	0.15	0.03
CE	26	93	18.64	0.27	0.46	0.04	0.27	13.20	3.13	0.58	0.68
BM	22	65	31.01	0.52	0.88	0.08	21.84	5.45	1.24	0.46	0.54
LCR	22	66	28.07	0.24	0.39	15.89	8.50	1.91	0.42	0.13	0.59
WP	20	60	26.92	0.09	19.49	2.65	1.45	1.06	0.91	0.24	1.02
C	23	95	21.85	0.16	0.27	3.05	13.87	3.02	1.04	0.28	0.17
R	23	96	20.19	0.24	1.58	12.31	3.88	0.98	0.61	0.33	0.26
BR	80+	111	17.46	0.08	1.11	11.73	2.64	0.71	0.64	0.21	0.34
CR	26	78	26.45	0.07	0.39	6.89	14.64	3.14	0.81	0.17	0.35
P	28	86	22.66	0.23	1.13	14.42	5.35	1.52	0.01	0.00	0.00
1100ºC											
YE	80+	103	17.49	0.09	0.44	8.81	4.60	1.37	1.27	0.53	0.38
PS	80+	111	13.19	0.12	5.55	3.80	1.19	0.86	0.95	0.27	0.45
GE	80+	110	7.30	0.11	0.19	0.09	0.22	0.41	1.53	2.59	2.16
BM	80+	96	20.78	0.31	0.52	2.72	13.89	2.28	0.49	0.13	0.44
LCR	80+	98	20.12	0.18	4.07	12.18	2.14	0.58	0.27	0.10	0.60
WP	25	60	24.97	2.10	19.07	2.09	0.75	0.36	0.13	0.15	0.33
C	80+	115	15.35	0.10	0.18	2.64	9.11	1.63	0.93	0.32	0.44
R	80+	115	12.31	0.09	0.62	4.82	2.57	1.55	1.70	0.38	0.58
BR	80+	122	9.18	0.04	0.17	0.93	2.14	2.73	2.20	0.47	0.50
CR	80+	102	18.61	0.16	0.73	10.47	5.44	1.07	0.35	0.19	0.19
P	80+	110	14.24	0.11	6.03	5.03	1.18	0.54	0.55	0.31	0.49

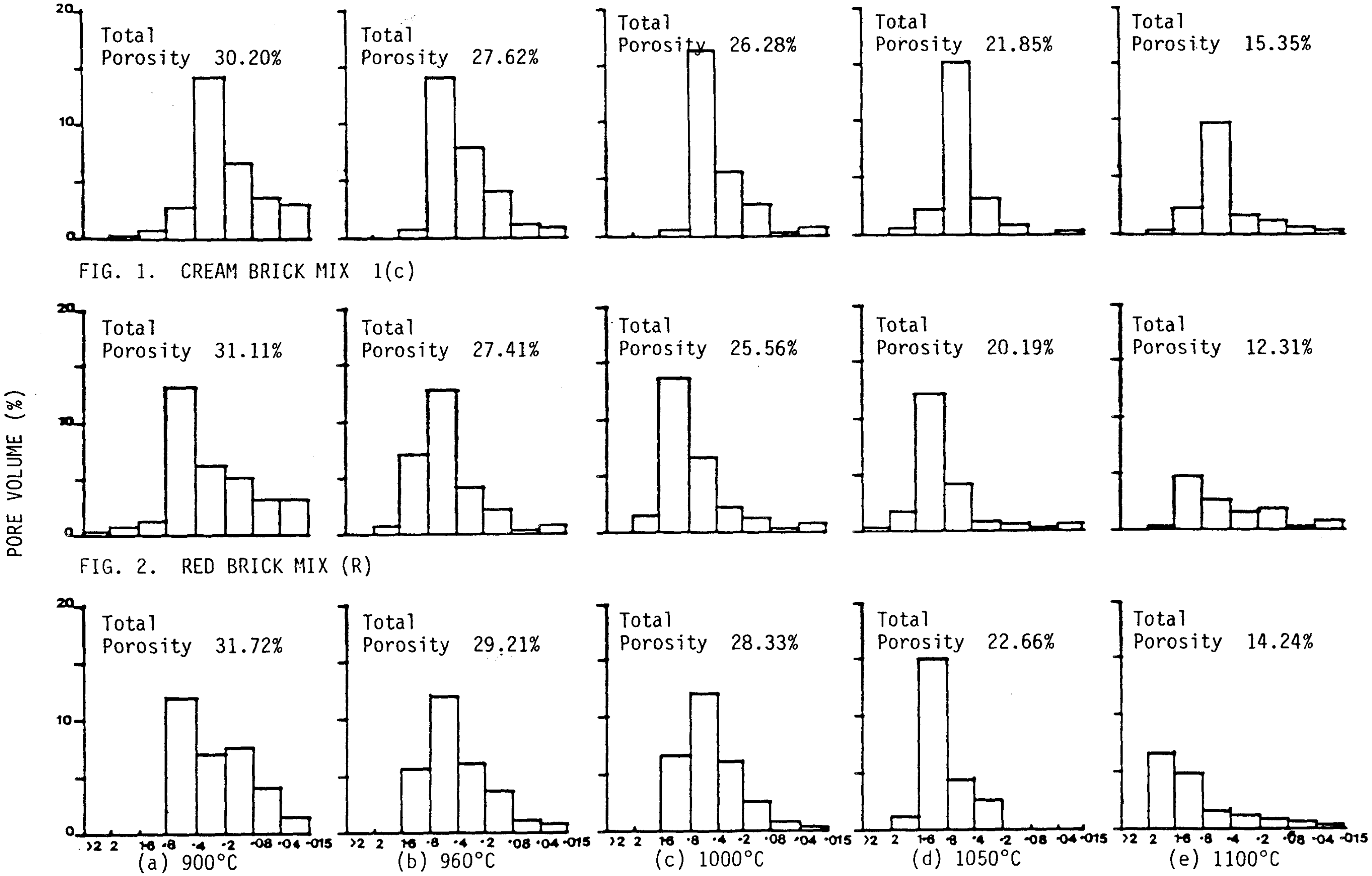


Figure 1. Cream brick mix (1c)

Figure 2. Red brick mix (R)

Figure 3. Pink brick mix (P)

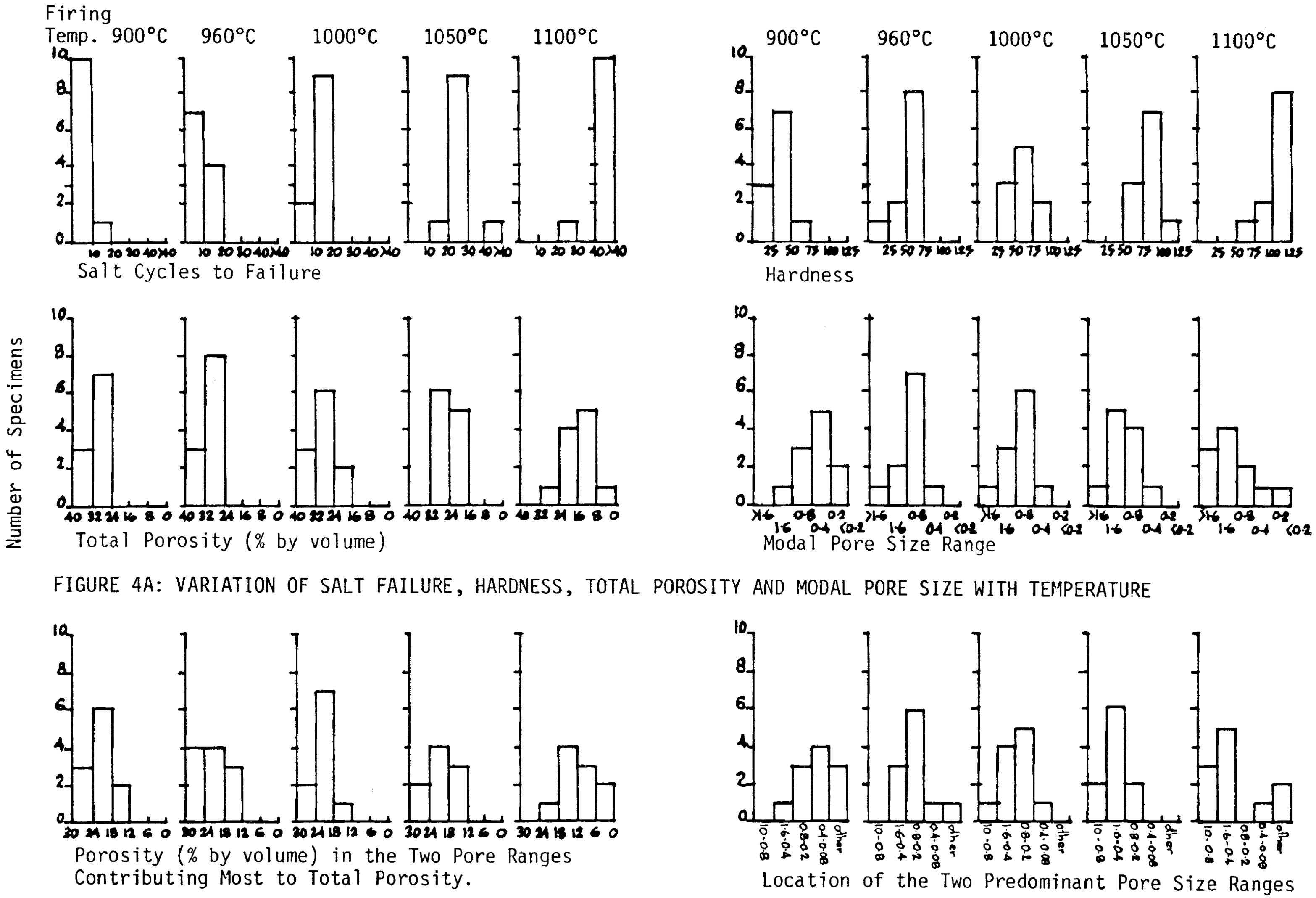
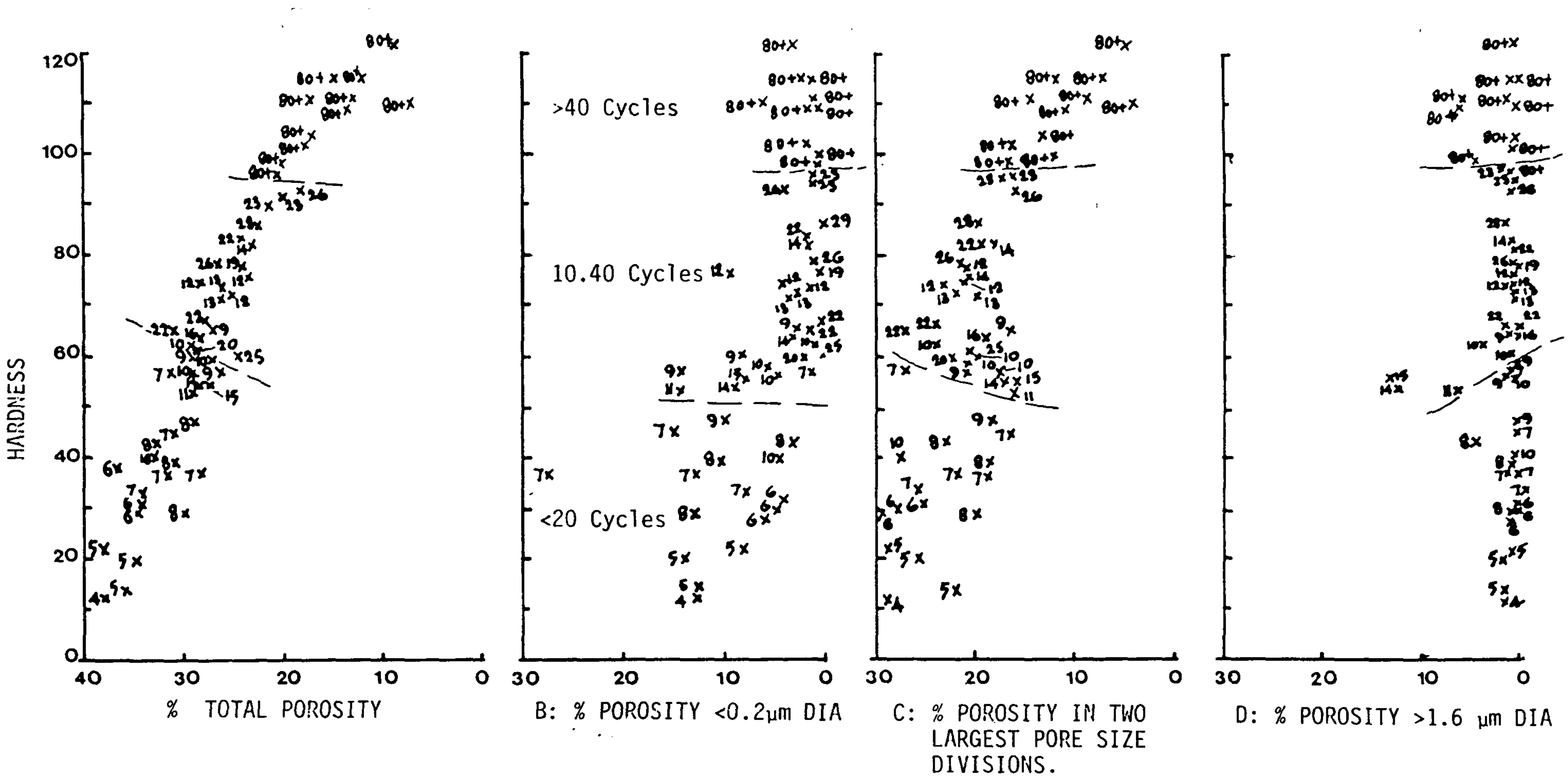


Figure 4A. Variation of salt failure, hardness, total porosity and modal pore size with temperature

Figure 4B. Variation of the two predominant pore size ranges with temperature



(From left)
Figure 5A. Cycles to failure related to hardness and porosity;
Figures 5B, C and D. Salt cycles to failure related to hardness and pore size fractions