BEHAVIOR OF CEMENTITIOUS MATERIALS IN A REPOSITORY ENVIRONMENT

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Needed Knowledge for Cementitious Materials in Tuff Repository Environment

Physical/mechanical properties in
  thermal environment
  durability
Shorter term and through post-closure period
Interaction with host rock
Interaction with waste package
pH control
Concrete carbonation
Other durability issues
Tailoring cementitious materials for
  optimium performance
  (knowledge needed for
  assurance).

TABLE I
BULK CHEMICAL COMPOSITION OF GROUTS

	Grout (wt %)	
Oxide	82-22	84-12
SiO_2	64.16	61.98
Al_2O_3	4.50	4.19
Fe_2O_3	2.74	1.10
CaO	25.88	27.52
MgO	1.83	4.65
MnO	0.12	0.17
Na_2O	0.10	0.10
K_2O	0.48	0.27
P_2O_5	0.11	0.02
Total	99.92	100.00

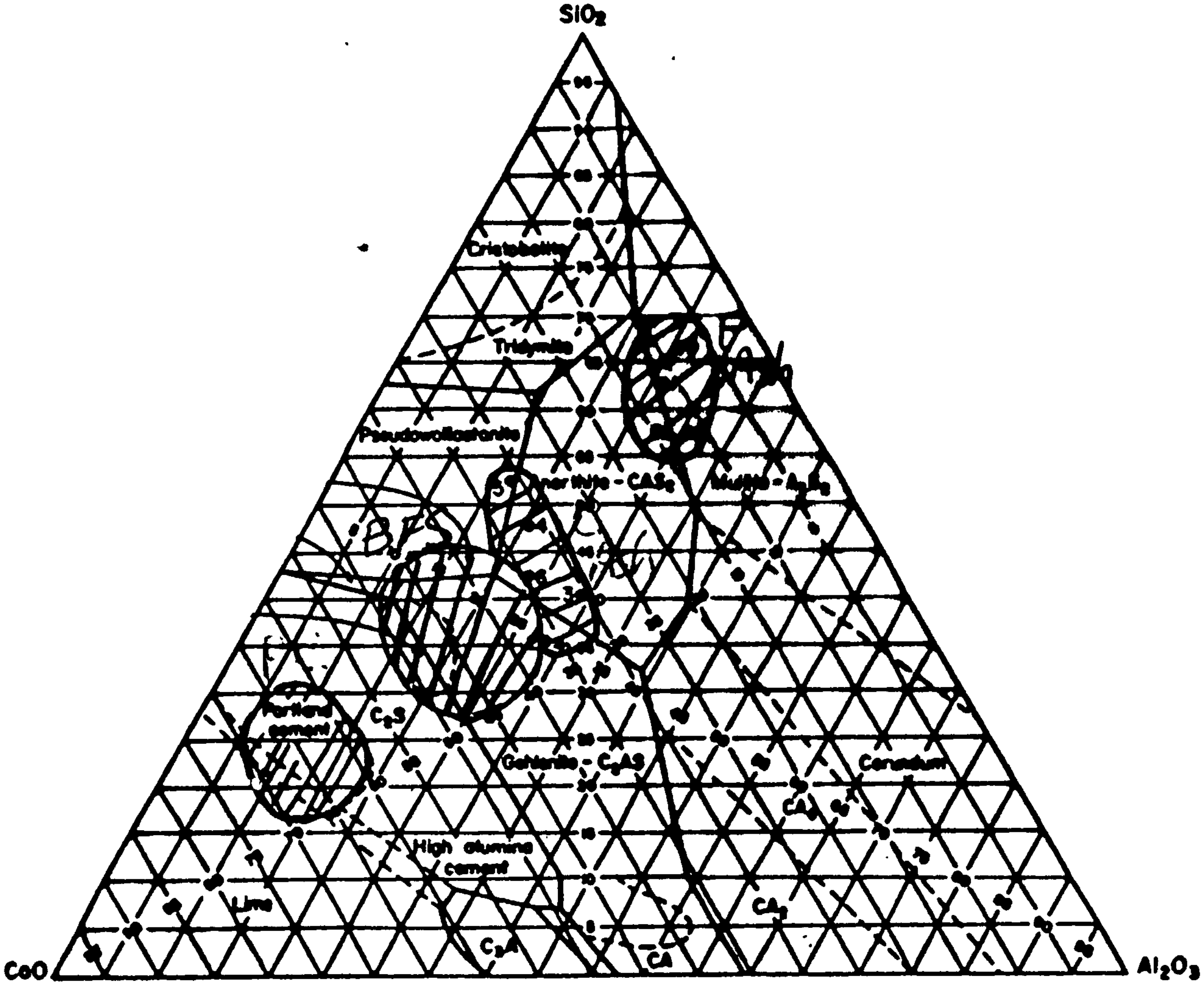
TABLE II
BULK CHEMICAL COMPOSITIONS OF GROUTS WITHOUT SAND AGGREGATE

	Grout (wt %)	
Oxide	82-22	84-12
SiO_2	38.60	48.45
Al_2O_3	7.74	5.44
Fe_2O_3	4.72	1.59
CaO	44.59	37.69
MgO	3.14	6.05
MnO	0.04	0.22
Na_2O	0.15	0.13
K_2O	0.83	0.40
P_2O_5	0.18	0.04
Total	99.99	100.01

APPLICATION AREAS

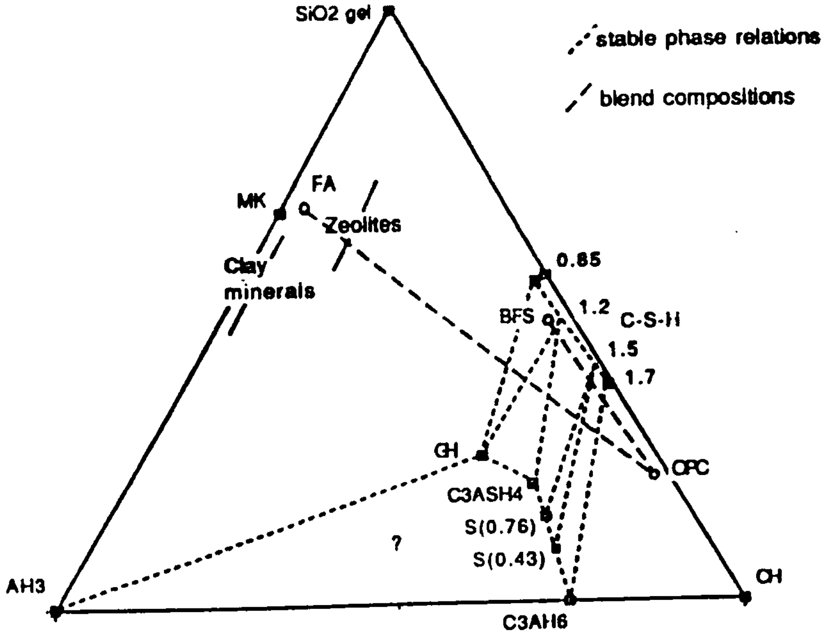
Application	Desirable Characts.
Matrix Mat.	Potential to condition *E*h and pH. Resistance to aggressive disposal conditions.

The System CaO-SiO$_2$-Al$_2$O$_3$

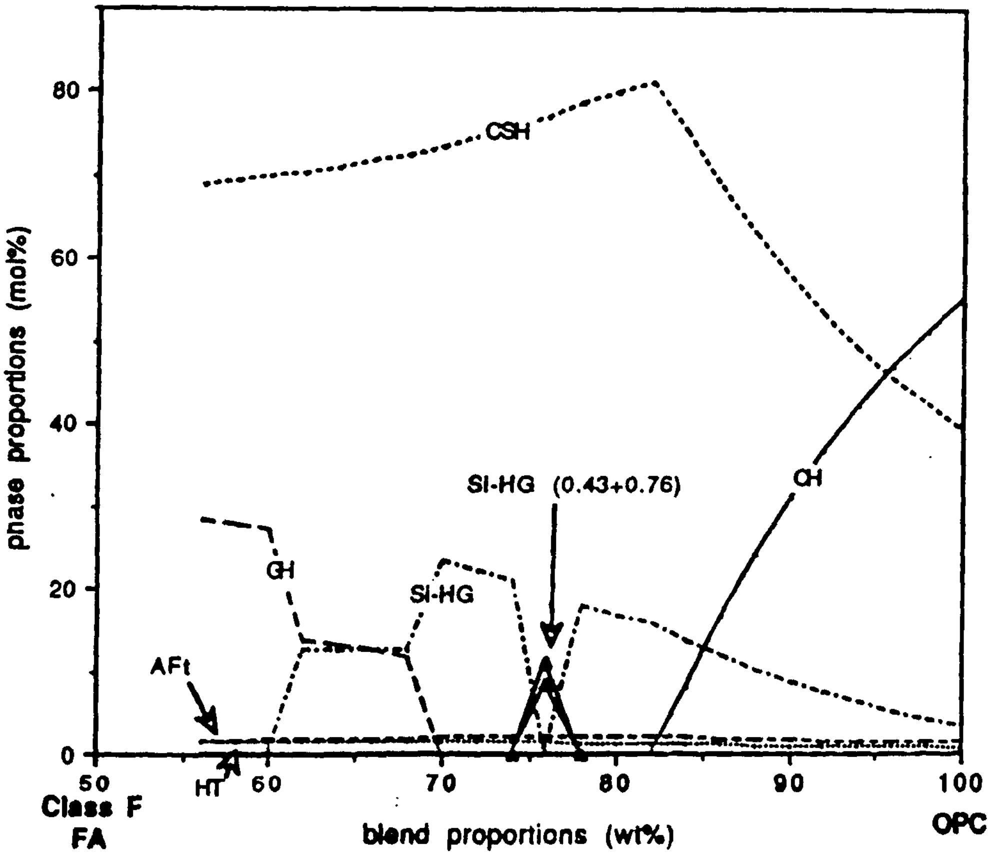


Phase	Constitution	Notes
Crystalline	$C_3A.3C\bar{S}.32H$	
Ettringite	$3CaO.Al_2O_3.3CaSO_4.32H_2O$	Potential substitution of Fe for Al, and various anions for S.
	$C_3A.C\bar{S}.12H$	
Monosulphate	$3CaO.Al_2O_3.CaSO_4.12H_2O$	As above.
	C_3AH_6	
Hydrogarnet	$3CaO.Al_2O_3.6H_2O$- $3CaO.Al_2O_3.SiO_2.4H_2O$	Potential substitution of Fe for Al and SiO_2 for H_2O.
Portlandite	$Ca(OH)_2$ CH	-
Hydrotalcite	$4MgO.Al_2O_3.10H_2O$	Potential substitution of various anions for $(OH)_2$.
Amorphous		
C-S-H	$(0.9\text{-}1.7)\ CaO.SiO_2.xH_2O$	Ca/Si ratio ~1.7 in OPC, but less i siliceous blends. Anion sorption increases with increasing Ca/Si ratio. Converse for cations.

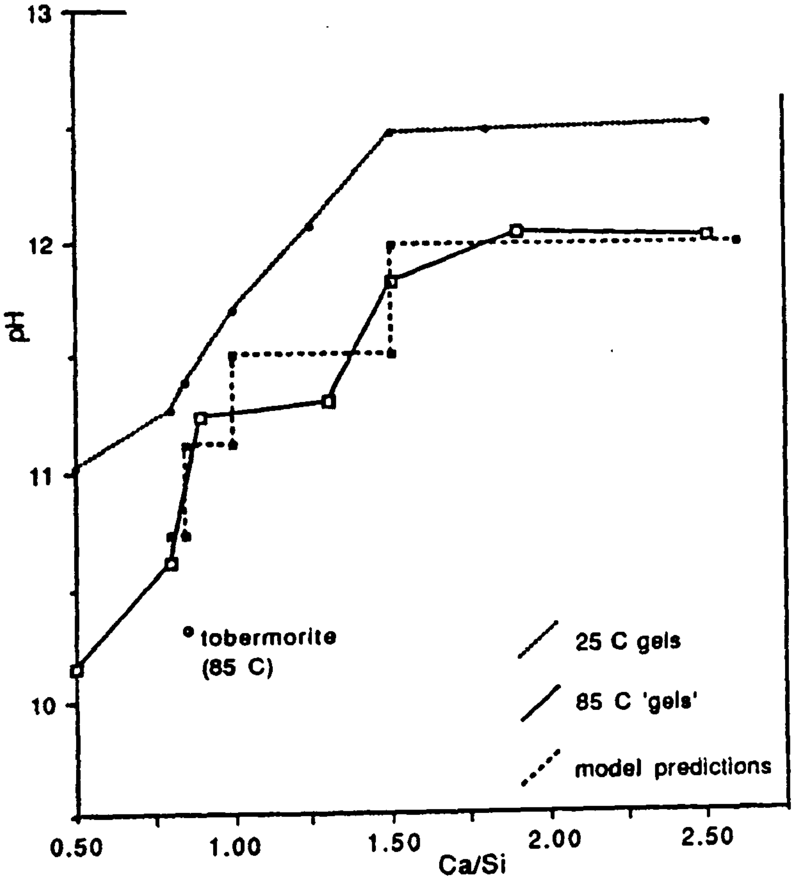
Cement hydrate phases: composition and properties.



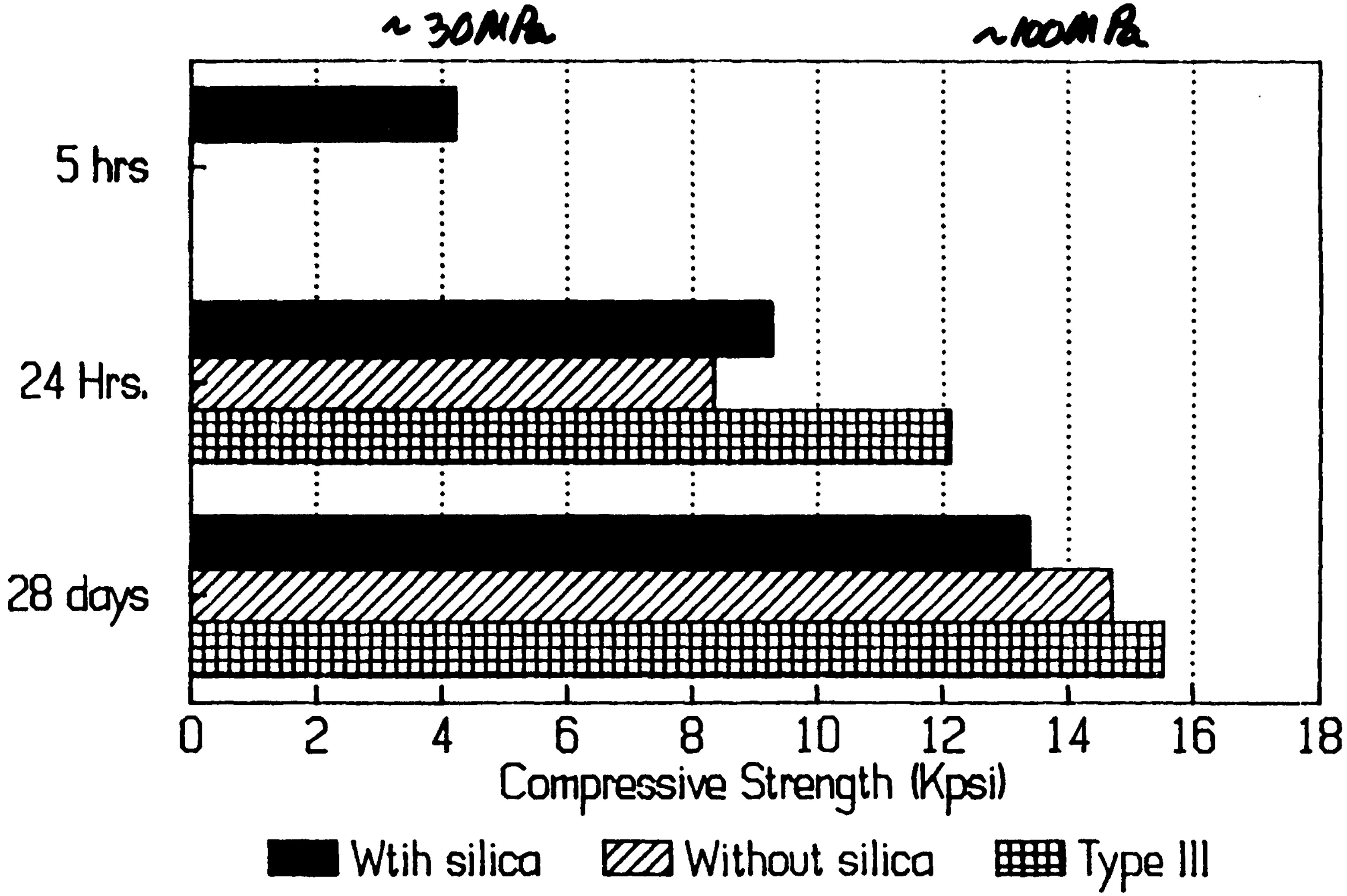
Phase relations in the water saturated portion of the C-A-S system at 25°C



Predicted stable phase assemblages as a function of blend proportion in an example

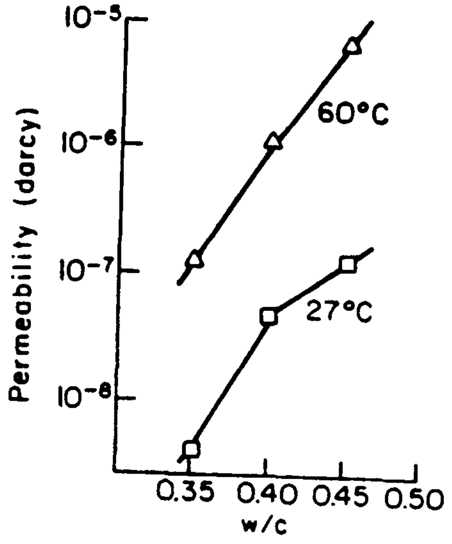


pH as a function of Ca/Si ratio in the C-S-H system.

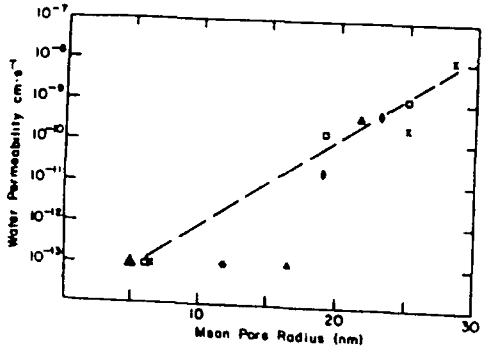


~30MPa

~100MPa



Relationship between permeability and w/c

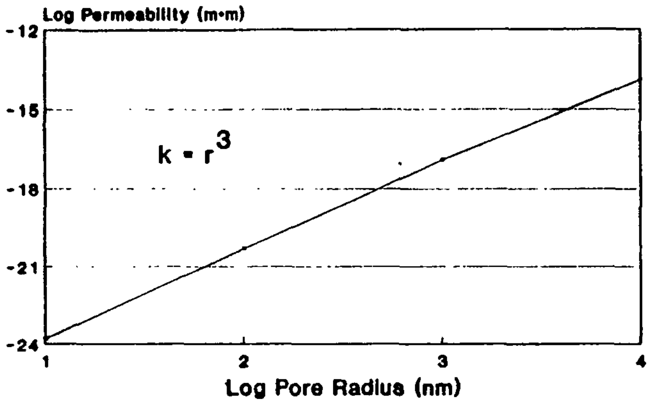


Water permeability vs.mean pore radius of pastes

PENNSTATE

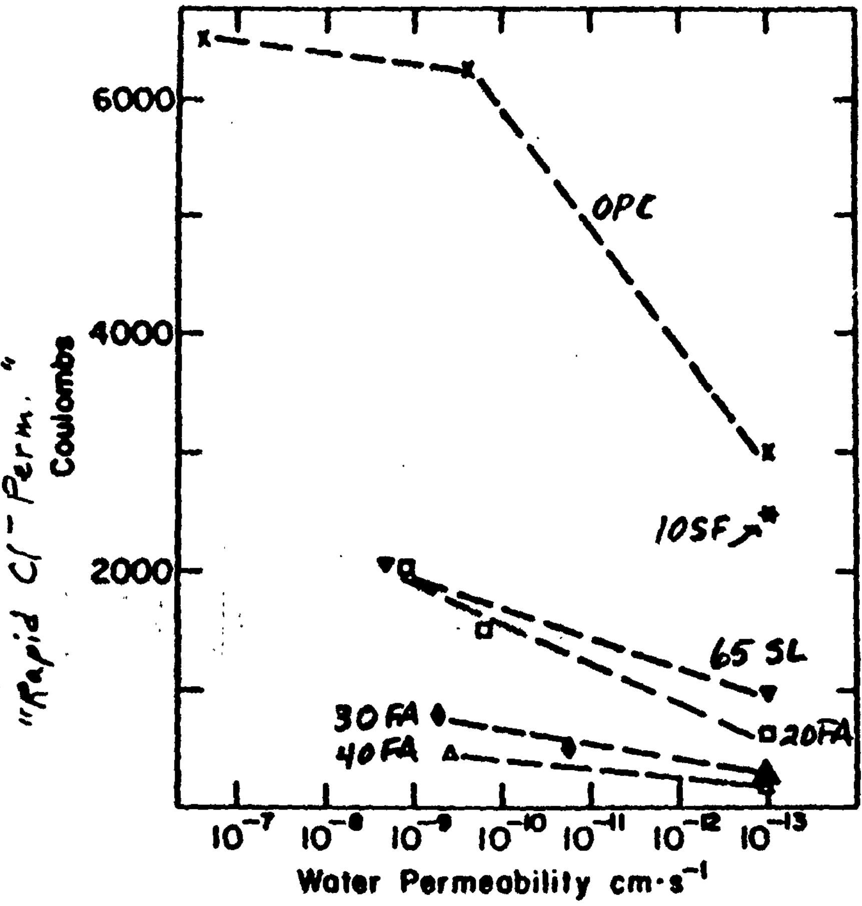
PERMEABILITY vs. POROSITY

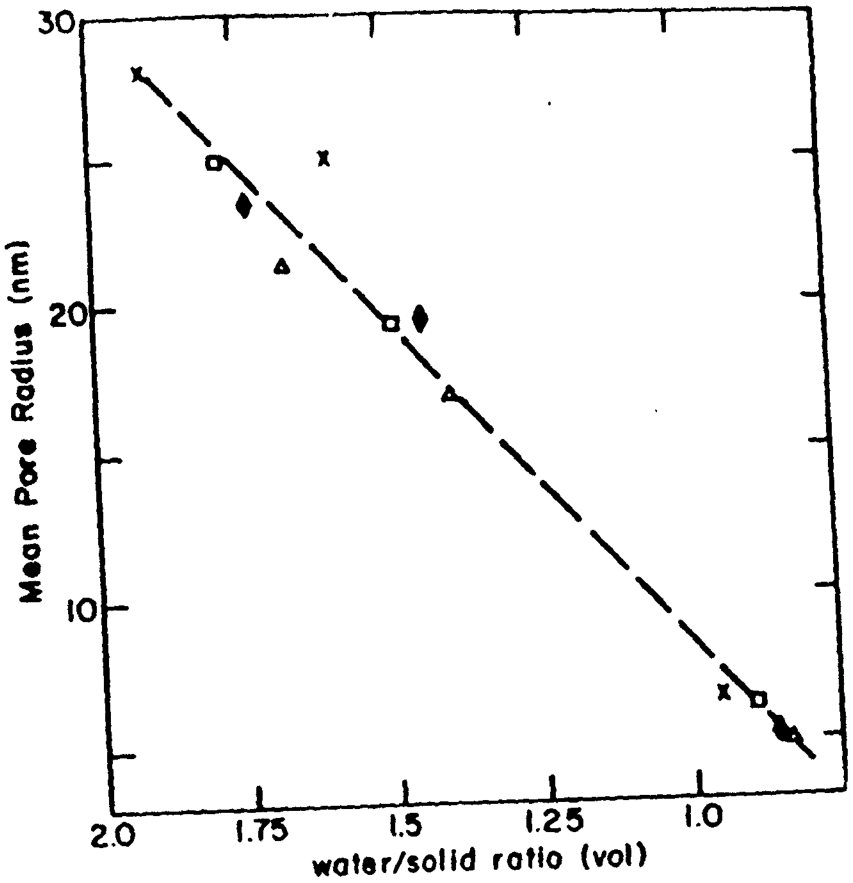
OPC pastes



(Atkinson and Hearne, 1984)

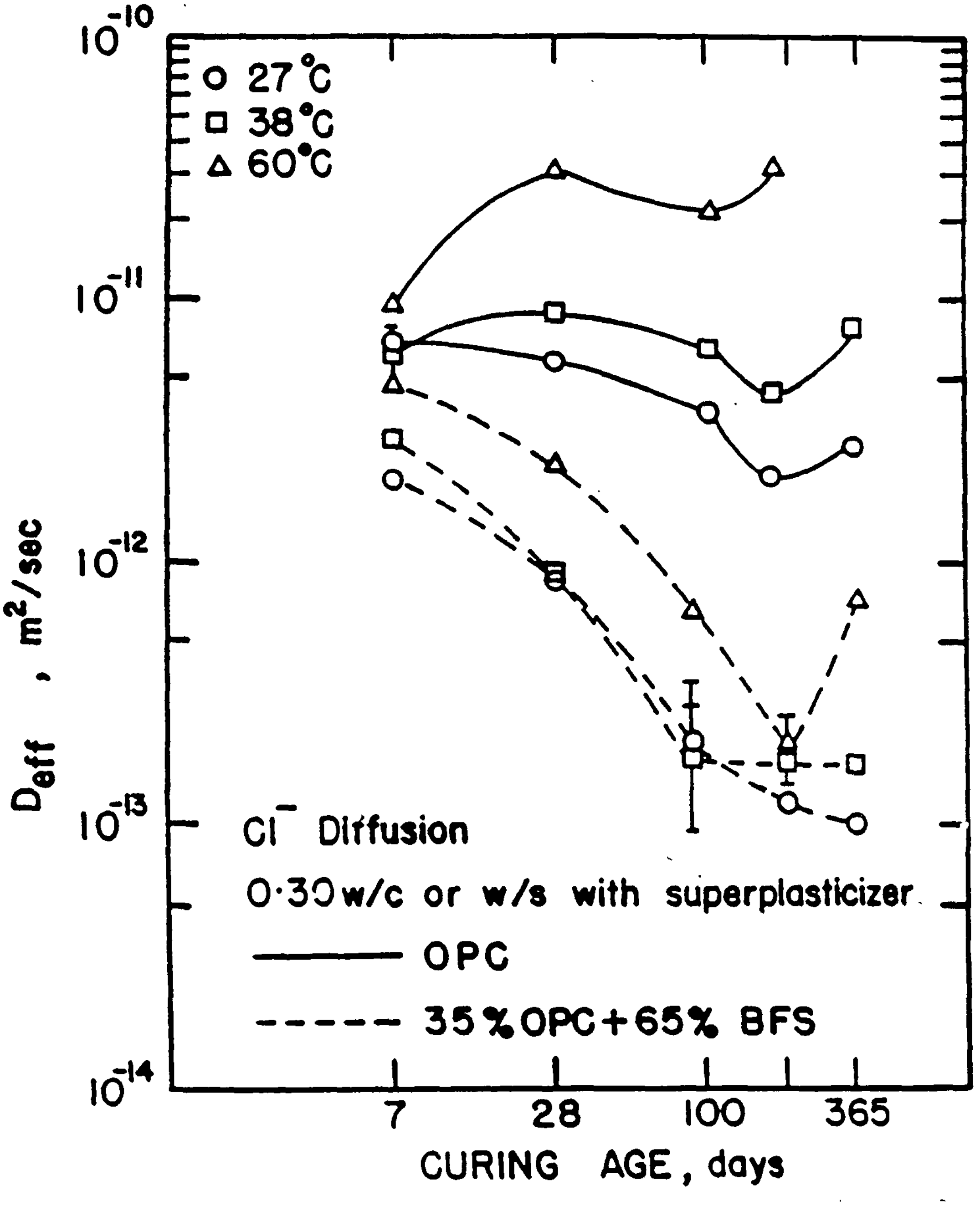
Cl "Diffusion/Permeability"





(includes OPC, SLAG, SF, FA)

EFFECTIVE DIFFUSIVITY OF CL⁻ IONS IN OPC vs. SLAG CEMENTS



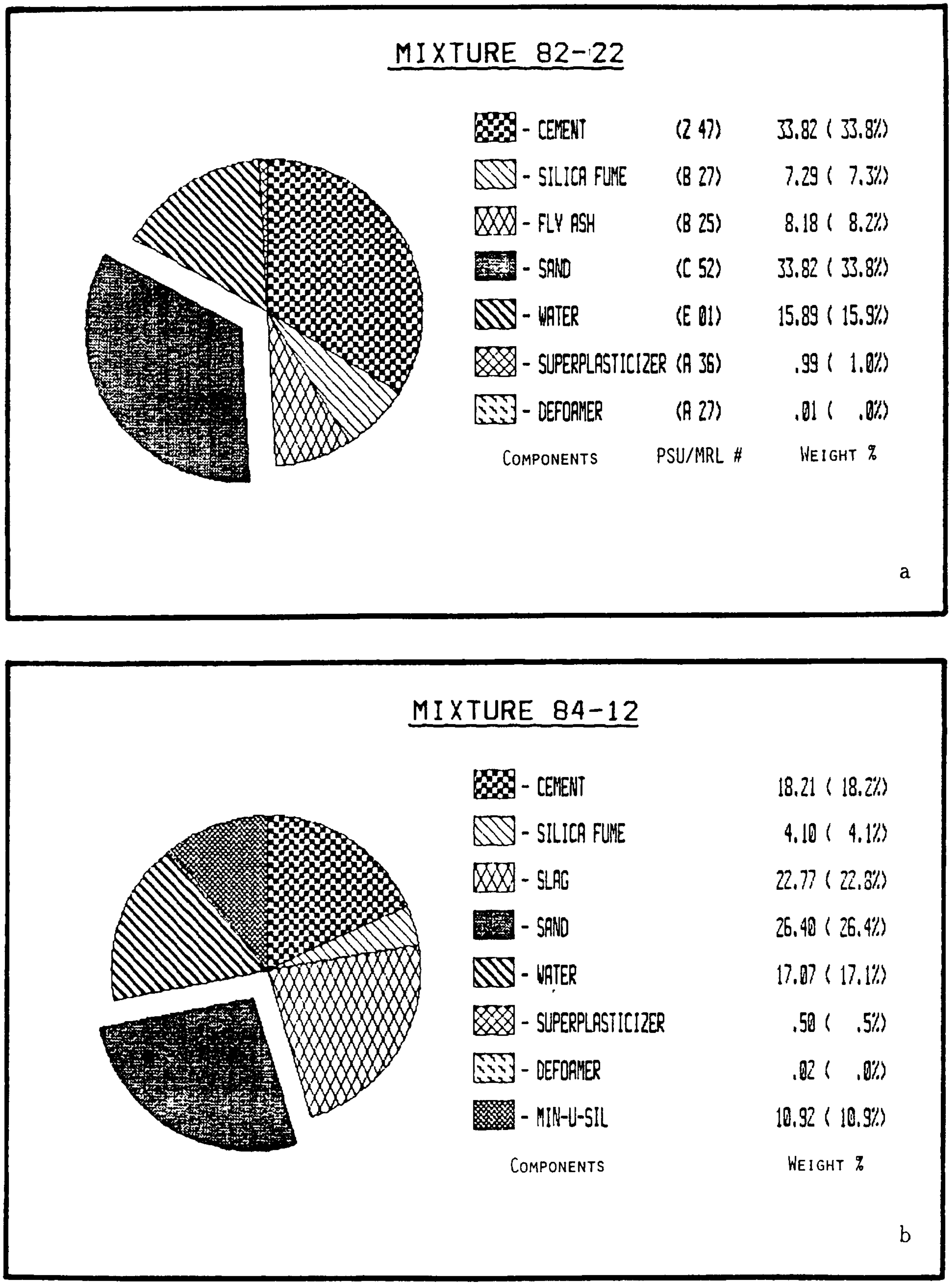


Fig. 1. Schematic representation of (a) 82-22 mortar and (b) 84-12 grout compositions.

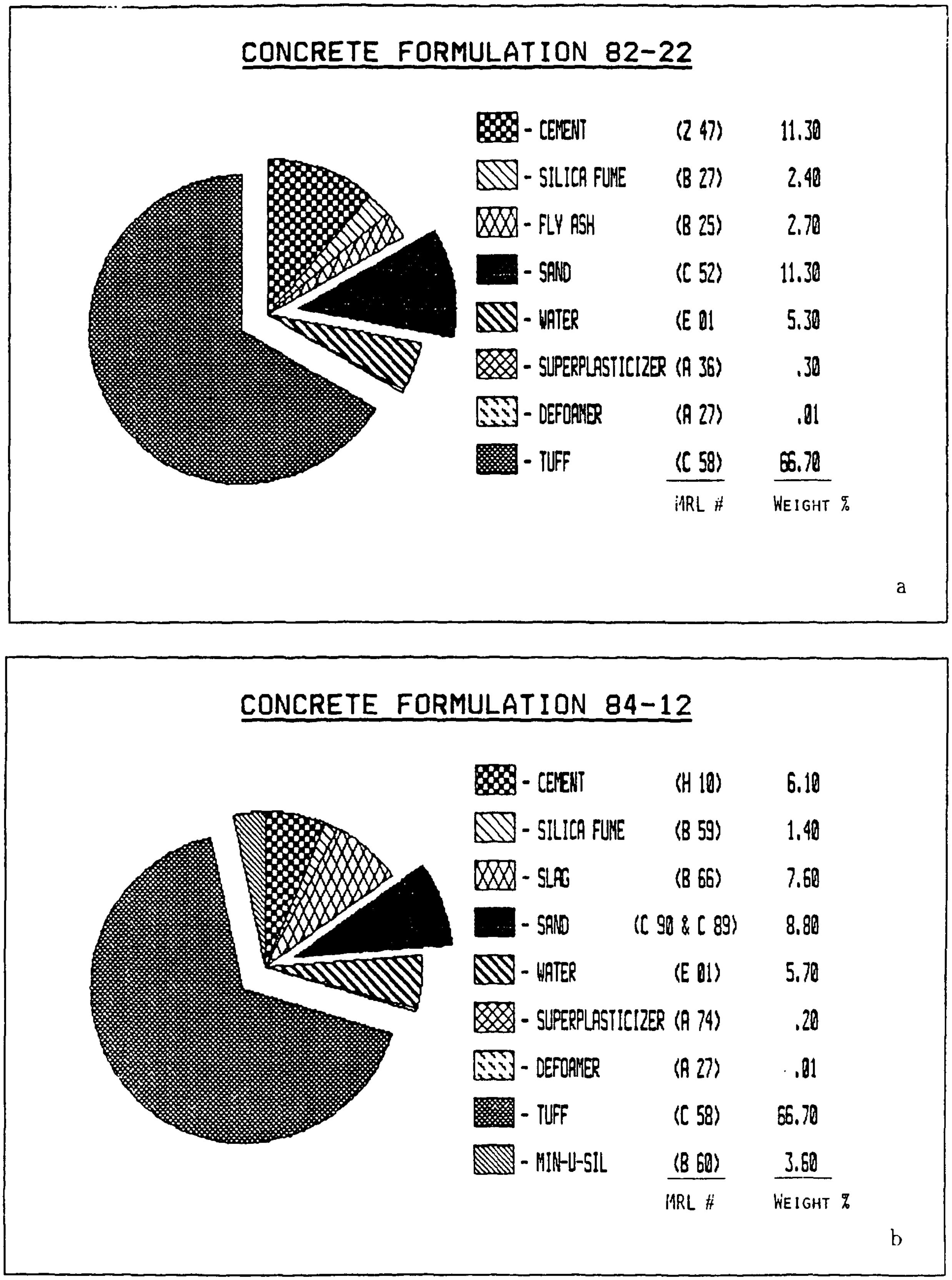


Fig. 2. Schematic representation of "artificial" concrete formulation based upon (a) 82-22 and (b) 84-12.

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Table 10. Water Permeabilities (Darcy) of Nonexpansive and Expansive Mortars

Curing Time (days)	Nonexpansive				Expansive			
	Curing Temperature (°C)							
	38		60		38		60	
	82-19	82-20	82-19	82-20	82-22	82-31	82-22	82-31
7	$<10^{-8}$	1.9×10^{-7}	$<10^{-8}$	$<10^{-8}$	$<10^{-8}$	$<10^{-8}$	$<10^{-8}$	$<10^{-8}$
14	$<10^{-8}$	$<10^{-8}$	$<10^{-8}$	$<10^{-8}$	--	--	--	--
28	$<10^{-8}$	$<10^{-8}$	$<10^{-8}$	$<10^{-8}$	$<10^{-8}$	$<10^{-8}$	$<10^{-8}$	5.5×10^{-7}

Table 14. Unconfined Compressive Strength (MPa) of Mixture 82-22

Curing Time (days)	Curing Temperature (°C)		
	38	60	90
7	103.31(1)*	--	119.5(3) [8.79]
28	127.6(3) [5.58]	137.3(1)	114.0(3) [3.75]
56	112.6(2) [9.21]	--	113.2(2) [12.42]
90	88.5(2) [6.72]	--	103.4(1)
180	130.95(2) [2.78]	130.71(3) [8.29]	--
360	62.4(2) [8.77]	60.4(2) [2.91]	124.0(1)
720	122.0(1)	--	--

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*Number of samples tested in ( ); one standard deviation, 1σ, in [ ].

TABLE 2--UNCONFINED COMPRESSIVE STRENGTHS (MPa) OF 82-22 SAMPLES HEATED AT 150 C AND 300 C

Heating Time	HYDROTHERMAL HEATING		"DRY" HEATING		
	Temperatures				
	150°C	**300°C**	**150°C**	**300°C**	**38°C**
7 days**	111 ± 12	112 ± 8	79 ± 10	37*	
28 days**	119 ± 3	95 ± 7	114 ± 2	44 ± 2	
28 days+	91	51			
Curing Time					
56 days++					110 ± 6

*visible cracks existed on each specimen.
**pre-curing at 38°C for 28 days prior to heating.
+precured at 38°C in $Ca(OH)_2$ solution for 900 days.
++baseline data specimens cured a total of 56 days at 38°C in $Ca(OH)_2$ solution.

TABLE 5--PERMEABILITY OF "DRY" AND "WET" THERMALLY TREATED 82-22 GROUT SAMPLES (Darcy)*

	"DRY" HEATED		**HYDROTHERMALLY HEATED**	
	150°	**300°**	**150°**	**300°**
7 days	3.7×10^{-6}	5.7×10^{-4}	8×10^{-7}	1.2×10^{-5}
28 days	5.8×10^{-6}	1.6×10^{-3}	1.5×10^{-6}	1.0×10^{-5}
900 days		---	$<1.0 \times 10^{-8}$	4.8×10^{-6}

*1 darcy ≈ 10^{-3} cm/sec

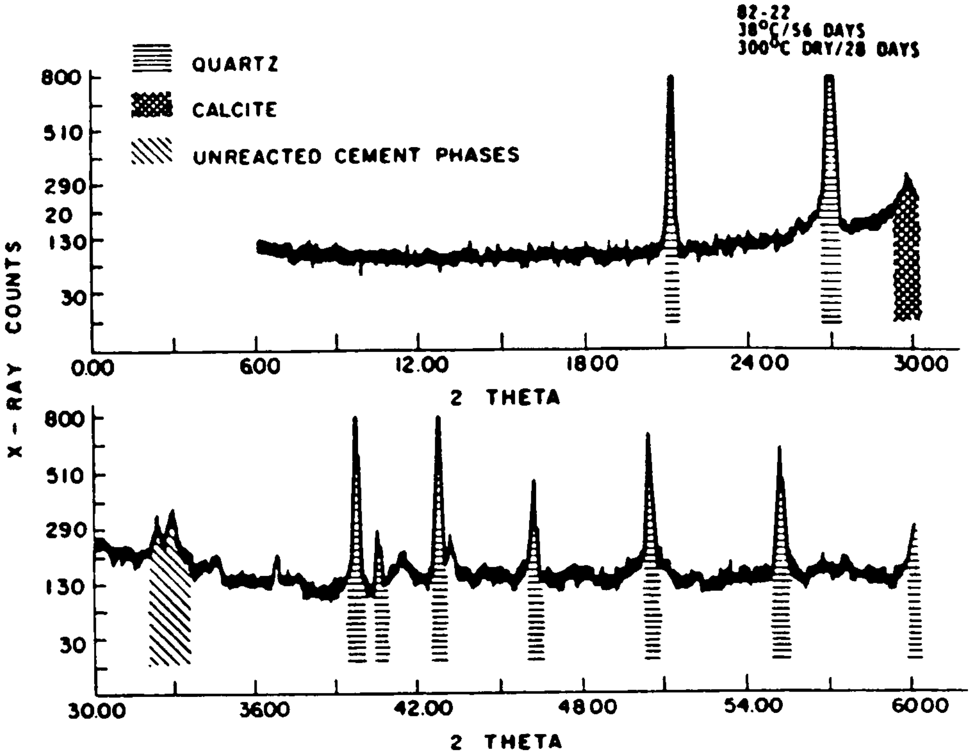


Fig. 4--X-ray diffractogram identifying all major phases (82-22 300 C for 28 days of "dry" heating)

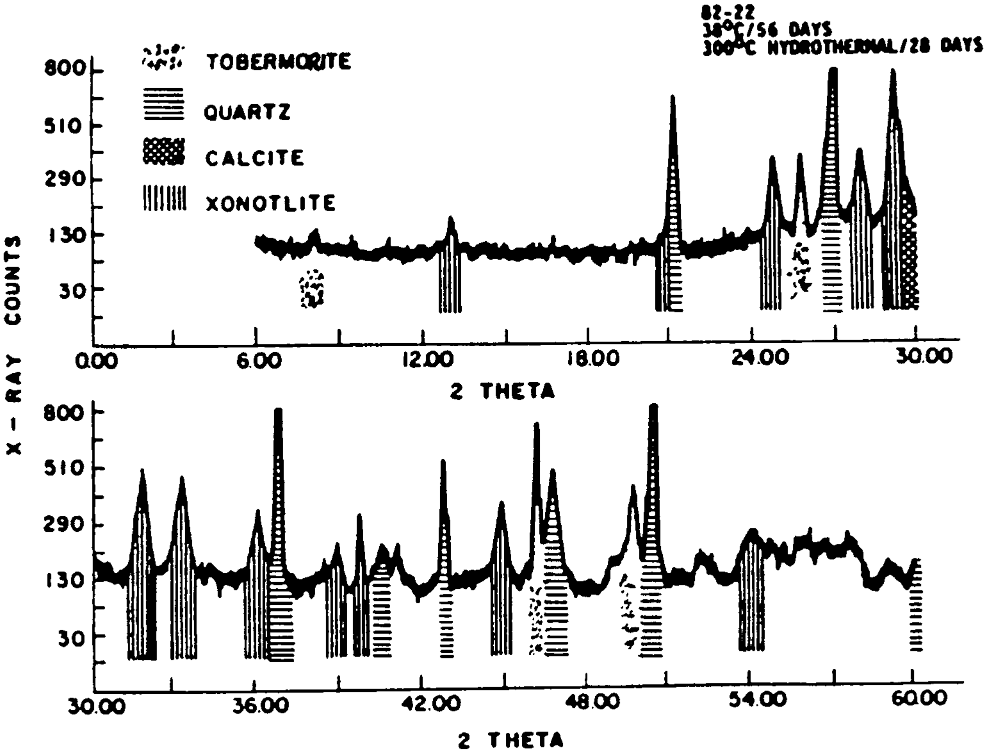
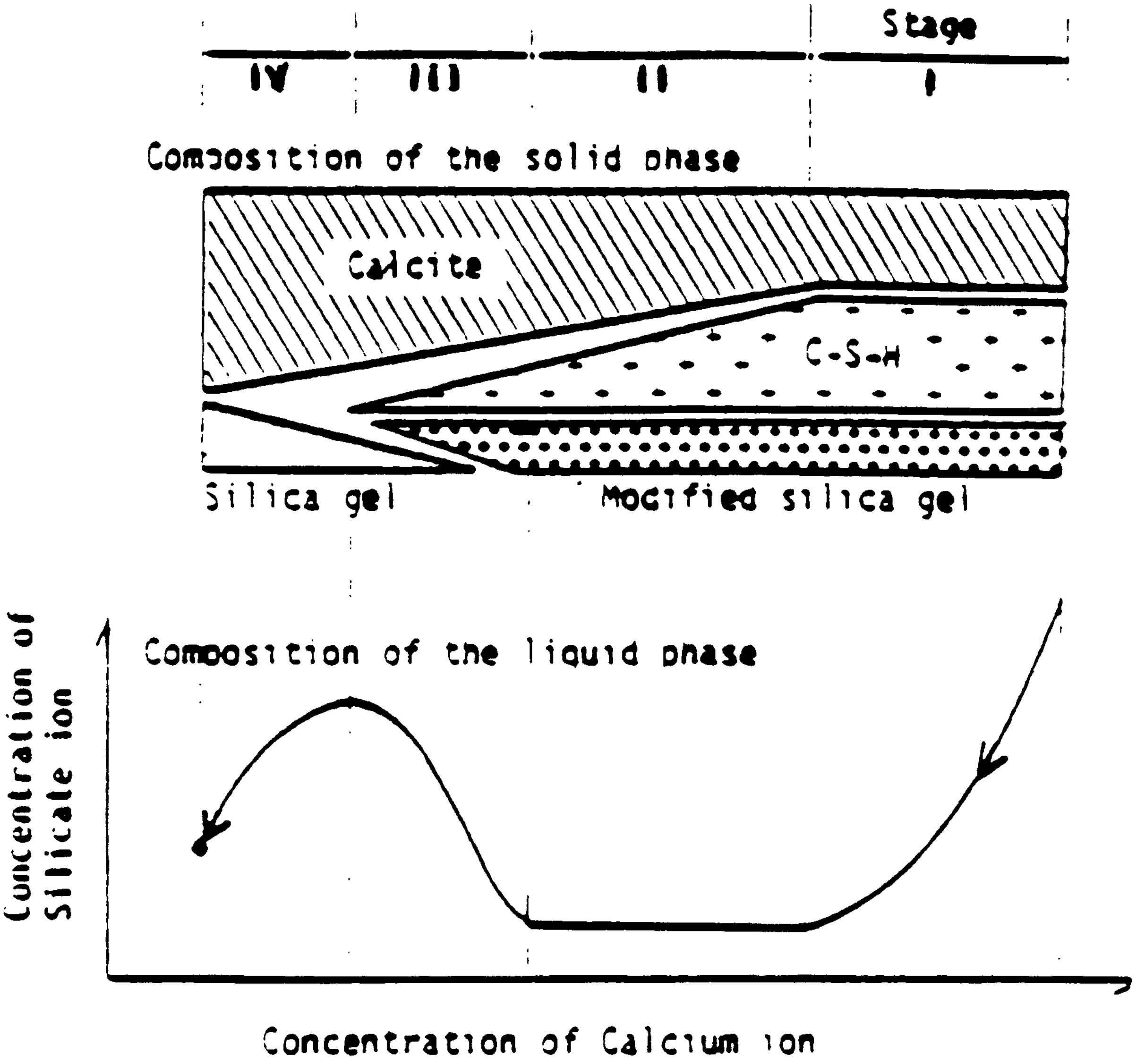


Fig. 7--X-ray diffractogram identifying all major phases (82-22 300 C for 28 days of "hydrothermal" heating)

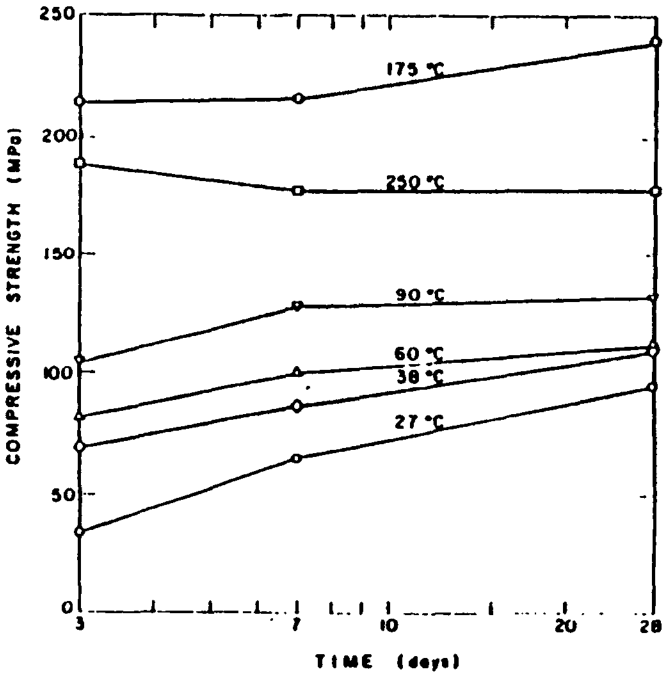
Other Effects - Carbonation

Calculated Results of the Carbonation Reactions of the Constituents of Cement Paste.

No. of Reactions	Equations of Reactions	ΔG^0_{298} of reactions [kcal/ml]	P_{CO2} equilibrium values [atm]
1	1/5 ($5CaO \cdot 6SiO_2 \cdot 5.5H_2O$) + (sol) + CO_2 (gas) = $CaCO_3$ (sol) + 6/5 SiO_2 (sol) + 1.1 H_2O (liq)	-11.29	$10^{-8.28}$
2	1/4 ($4CaO \cdot Al_2O_3 \cdot 19H_2O$) (sol) + CO_2 (gas) = $CaCO_3$(sol) + 1/2 $Al(OH)_3$ (am) + $4H_2O$ (liq)	-14.70	$10^{-10.78}$
3	1/3 ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) (sol) + CO_2 (gas) = $CaCO_3$ (sol) + $CaSO_4 \cdot 2H_2O$ (sol)	-10.26	$10^{-7.52}$
4	1/3 ($3CaO \cdot Fe_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) + CO_2 = $CaCO_3$ + $CaSO_4 \cdot 2H_2O$ + 2/3 $Fe(OH)_3$ + 23/3 H_2O	-14.07	$10^{-10.31}$
5	$Ca(OH)_2$ (sol) + CO_2 (gas) = $CaCO_3$ (sol) + H_2O (liq)	-17.82	$10^{-13.1}$



Carbonation stages (schematic) of C-S-H, prepared from solution



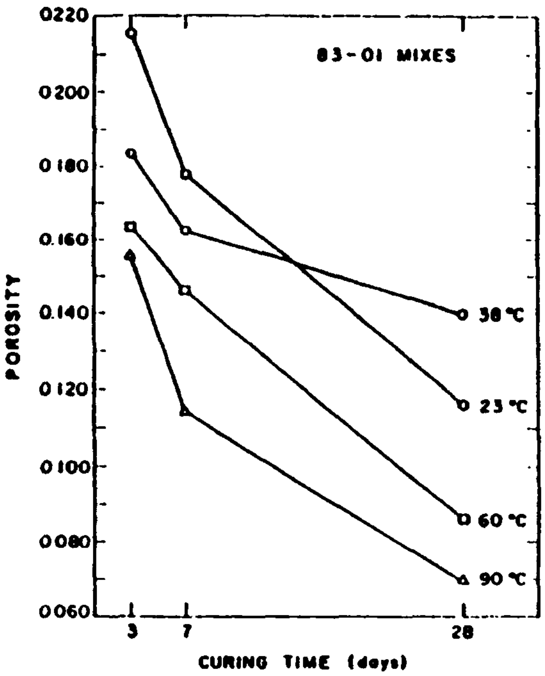
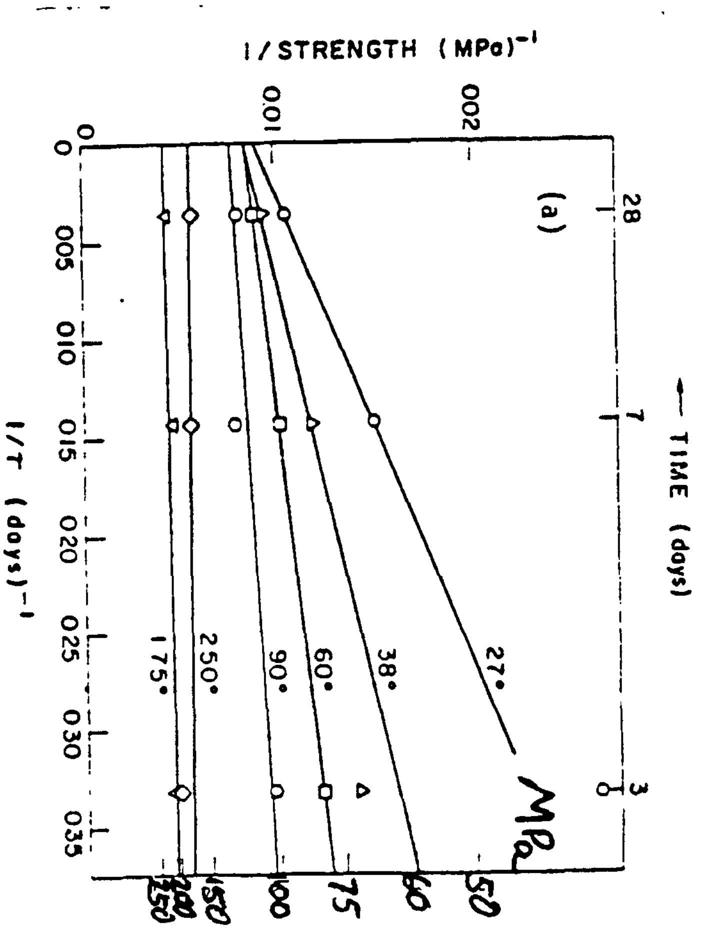


FIG. 4. Compressive strength of mortar mixtures 82-11 (top two) and 83-01 (bottom four) cured at constant temperatures from 27 to 250°C.

FIG. 5. Porosity (Hg porosimetry)-curing time and temperature relation for 83-01 slag-cement mixtures.



SUMMARY,

Physical constraints:

- Low permeability
- Mechanical stability
- Fine interwoven solid/pore structure

Environmental factors:

- Near equilibrium state may be attained (especially if elevated temperatures).

Summary

- Modest data base exists for concrete mechanical properties at elevated temperatures
- Potential durability appears to depend on several factors
    - --- physical/mechanical properties under sustained elevated temperatures
    - --- chemical compatibility of cementitious matrix with host rock; phase stability and effects on water chemistry
    - --- benign effects of cementitious materials on waste package
    - --- adequate matrix-aggregate bonding
- Specialized (tailored) cements/concretes appear feasible/in order