U.S. DEPARTMENT OF ENERGY
OFFICE OF CIVILIAN RADIOACTIVE WASTE MANAGEMENT

NUCLEAR WASTE TECHNICAL REVIEW BOARD
PANEL ON STRUCTURAL GEOLOGY & GEOENGINEERING

SUBJECT: GEOCHEMICAL CONSIDERATIONS IN SEALING

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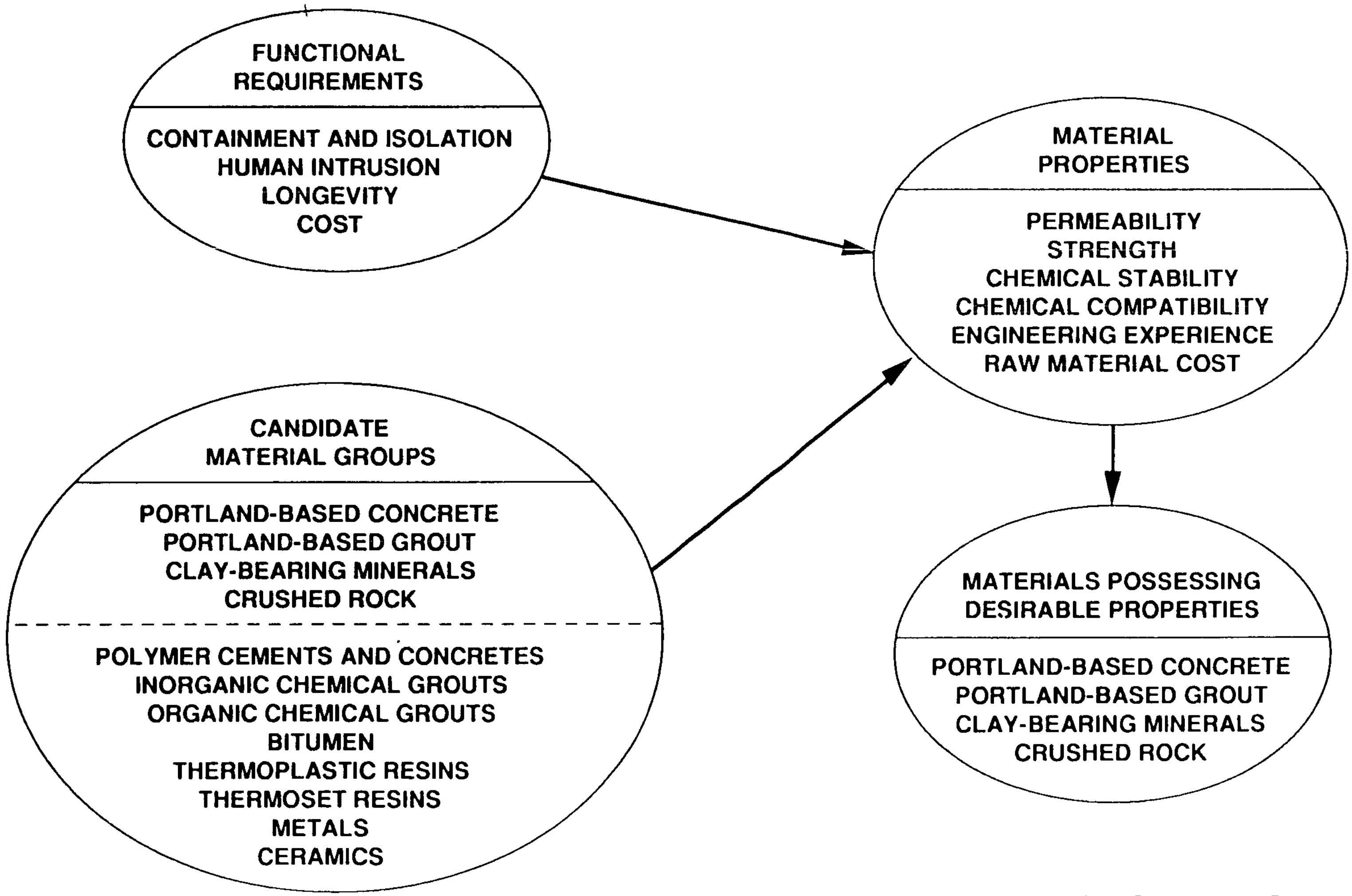
Overview of the Material Selection Methodology

<u>Process Consists of Repeated Material Evaluations</u>

- Qualitative comparison to seal functional and design requirements
- Quantitative comparison to specific design requirements
  - evaluation of material properties

- Future evaluations as seal requirements are refined
  - evaluation of material properties

Initial Material Screen



REFERENCE: SAND84-1895

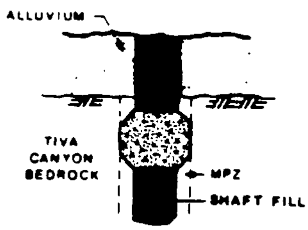
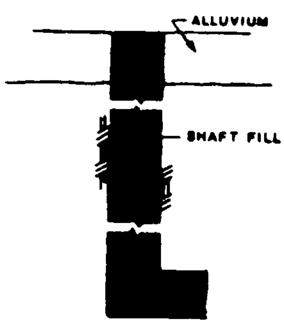
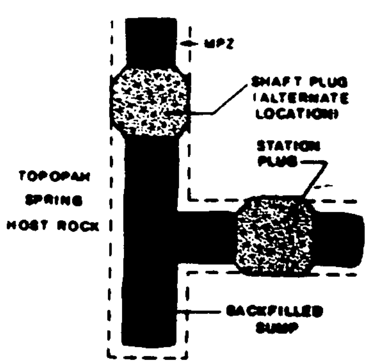
Second Material Evaluation

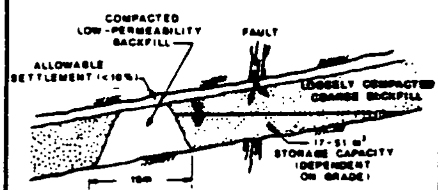
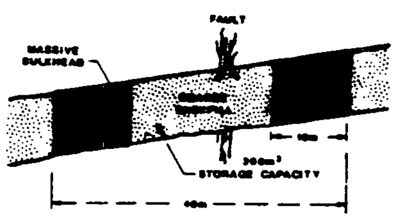
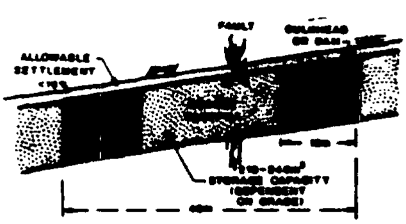
<u>General Design Requirements Developed For</u>

- Strength
- Emplacement considerations
- Seal-groundwater chemistry
- Environmental conditions

<u>Specific Design Requirements Developed For</u>

- Hydraulic conductivity

DESIGN OPTIONS	DESIGN REQUIREMENTS	CANDIDATE MATERIAL
 ANCHOR-TO-BEDROCK PLUG	■ K ≤ 10^{-5} TO 10^{-4} cm/s	■ STANDARD CONCRETE
 GENERAL SHAFT BACKFILL	■ K ≤ 10^{-2} cm/sec	■ CRUSHED TUFF
 STATION AND SHAFT PLUGS	■ K ≤ 10^{-6} to 10^{-5} cm/s	■ STANDARD CONCRETE OR COMPACTED EARTH

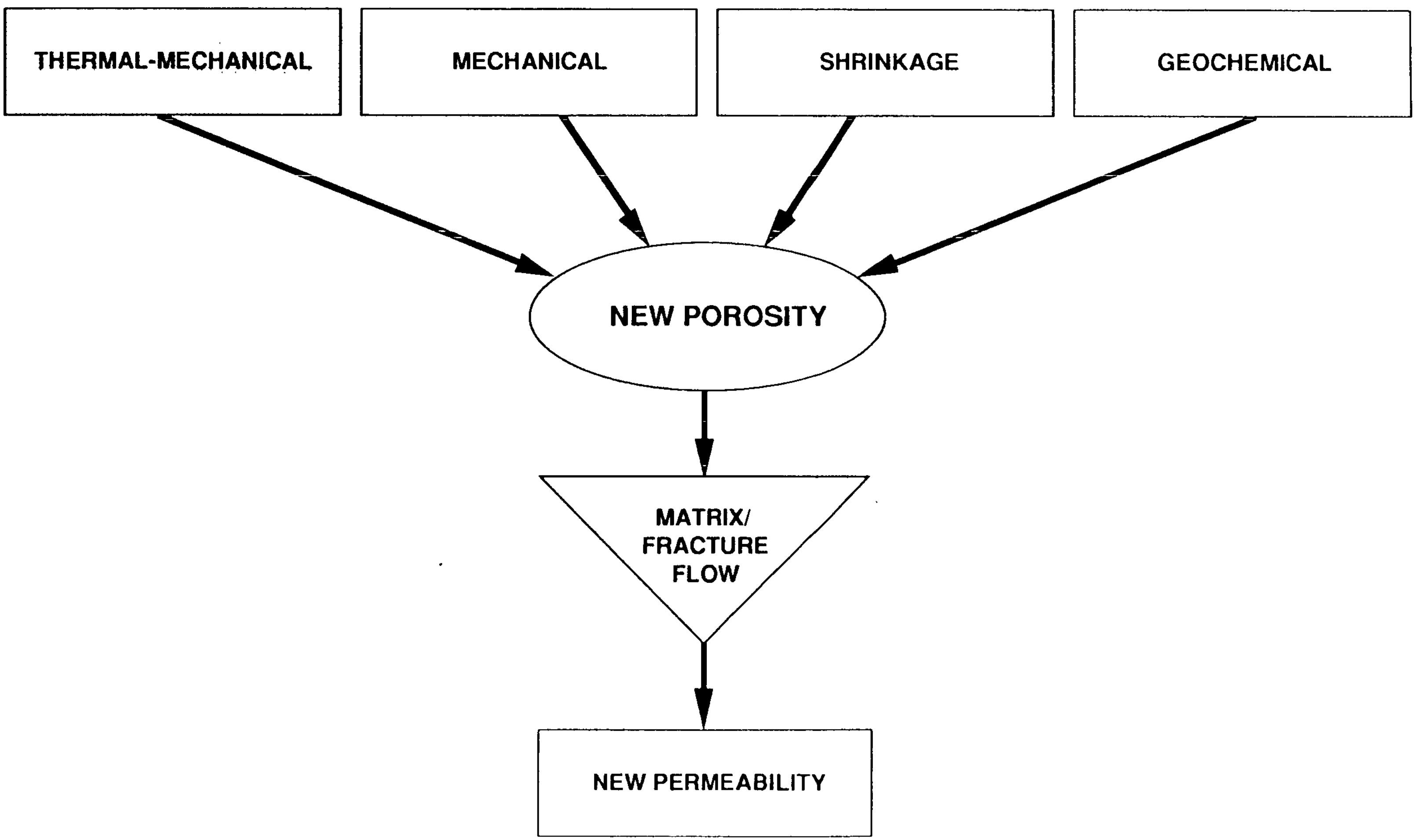
DESIGN OPTIONS	DESIGN REQUIREMENTS	CANDIDATE MATERIAL
 (A) SINGLE DAM OR SINGLE BULKHEAD WITH SETTLEMENT	■ EMPLACEMENT DRIFT $K \leq 10^{-5}$ TO 10^{-4} cm/s	■ COMPACTED EARTH OR HIGH-TEMPERATURE CONCRETE
	■ PERIMETER DRIFT OR MAINS $K \leq 10^{-4}$ cm/s	■ COMPACTED EARTH OR STANDARD CONCRETE
 (B) DOUBLE BULKHEAD (NO SETTLEMENT)	■ $K \leq 10^{-8}$ TO 10^{-7} cm/s	■ HIGH-TEMPERATURE CONCRETE OR COMPACTED EARTH
 (C) DOUBLE DAM OR DOUBLE BULKHEAD WITH SETTLEMENT	■ $K \leq 10^{-5}$ TO 10^{-4} cm/s	■ COMPACTED EARTH

Observed Properties of Candidate Seal Materials

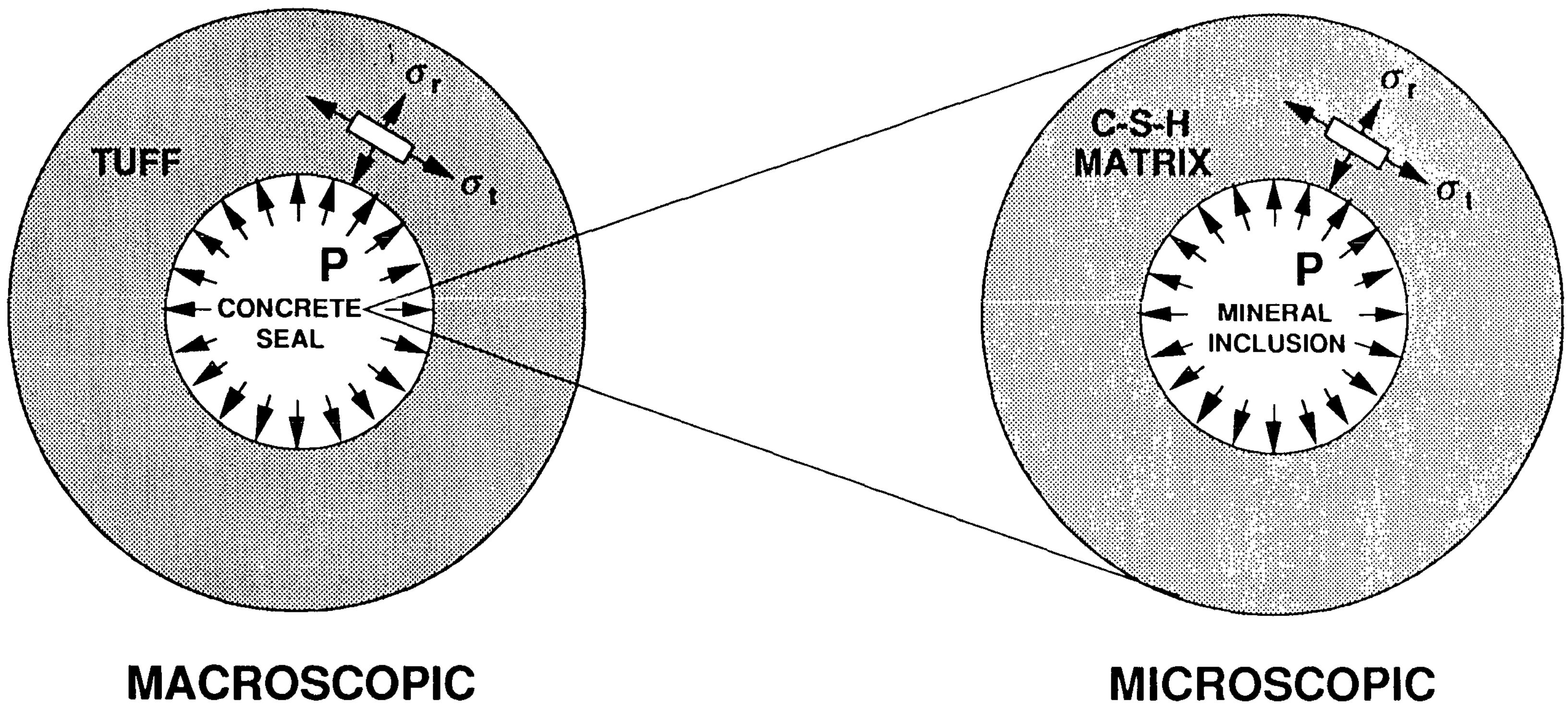
PROPERTY	CEMENTITIOUS MATERIALS	EARTHEN MATERIALS
HYDRAULIC CONDUCTIVITY	TYPICAL: 10^{-8}-10^{-6} $\frac{cm}{sec}$ BEST: 10^{-10} $\frac{cm}{sec}$	TYPICAL: 10^{-5} - 10^{+2} $\frac{cm}{sec}$ BEST: 10^{-10} $\frac{cm}{sec}$
STABILITY	CHEMICAL ALTERATION	DEHYDRATION
GROUNDWATER CHEMISTRY INTERACTIONS	INCREASED LEVELS OF OH^-, Na^+, K^+, $SO_4^=$, Si, and Ca^{++} STABILIZING EFFECT OF TUFF	INCREASED LEVELS OF Na^+, K^+, Ca^{++}, Mg^{++}, Si, Al CONCENTRATION INCREASES CONTROLLABLE
STRENGTH	HIGH CONTROLLABLE	CRACKING POTENTIAL SWELLING

Overview

Cementitious Sealing Material Degradation Model



Thermal-Mechanical Interactions



- **Differential expansion causes pressure**
- **Microscopic and macroscopic analyses based upon spherical/cylindrical analysis of Timoshenko and Goodier**

Thermal-Mechanical Interactions

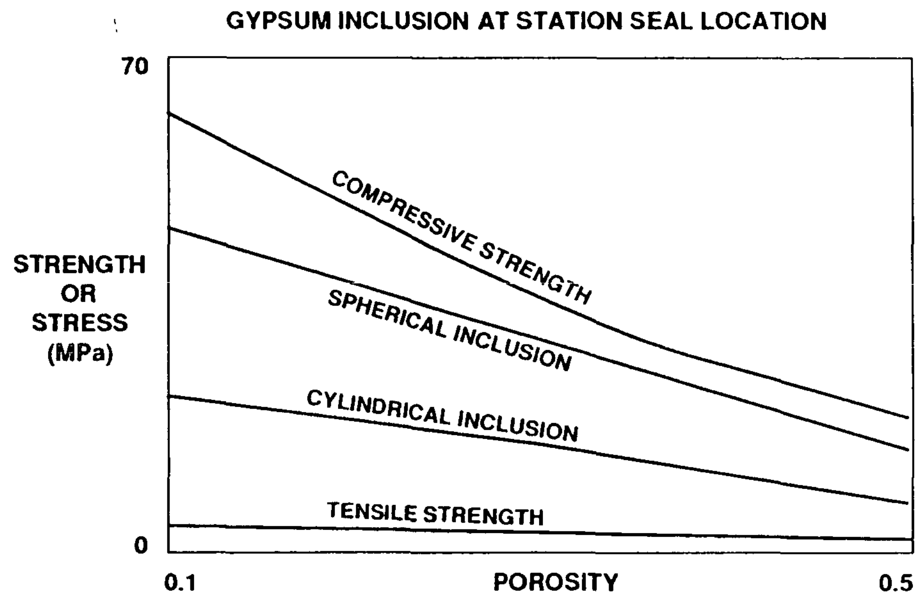
Microscopic Analyses

- **Microscopic inclusions in C-S-H Matrix**
  - Ettringite
  - Hydrogarnet
  - Portlandite
  - Silica
  - Gypsum
  - Unreacted cement phases
  - Fine aggregate
  - Coarse aggregate

- **Tensile stresses compared to**
  - Confining stress
  - Tensile strength

Thermal-Mechanical Interactions

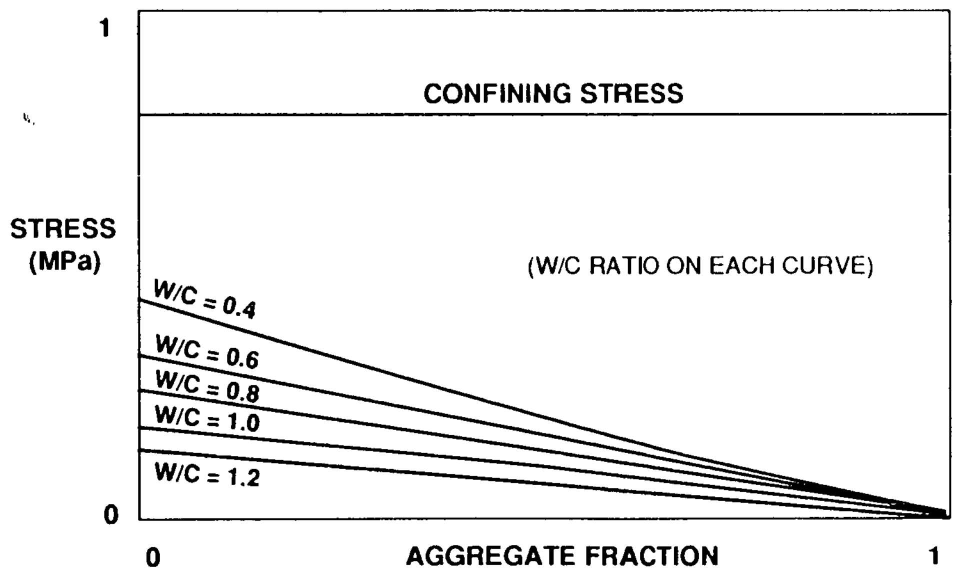
Microscopic Analyses



- Stress greater than tensile strength or confining stress
  - Plug unstable to thermal expansive stresses
- Similar results obtained for
  - Portlandite
  - Unreacted cement phases
- Amounts of gypsum, Portlandite, and unreacted cement phases must be controlled

Thermal-Mechanical Interactions

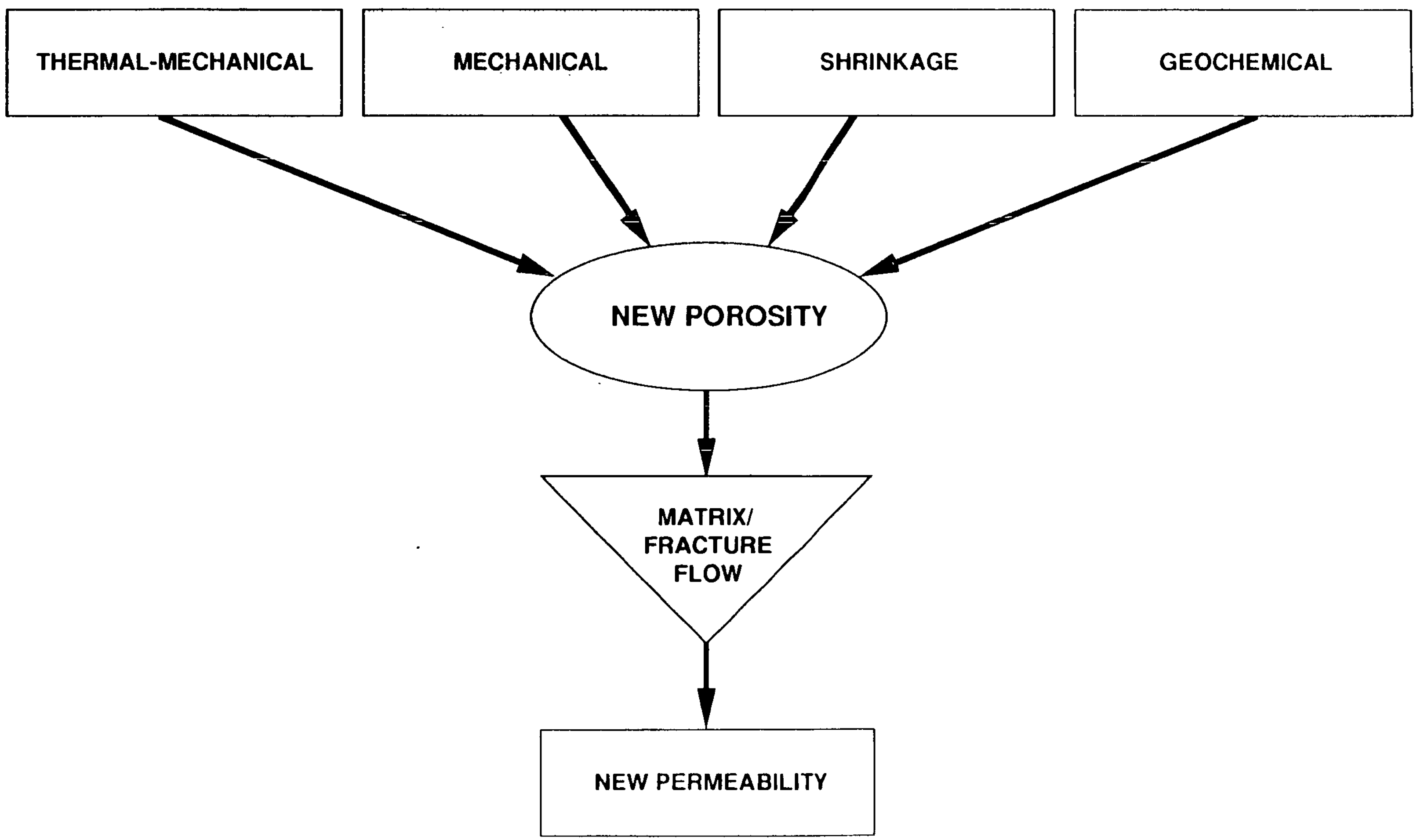
Macroscopic Effects
Anchor-to-Bedrock Seal



- Thermally-induced stresses less than half of confining stresses
- Similar results obtained for Station seal and Calico Hills seal

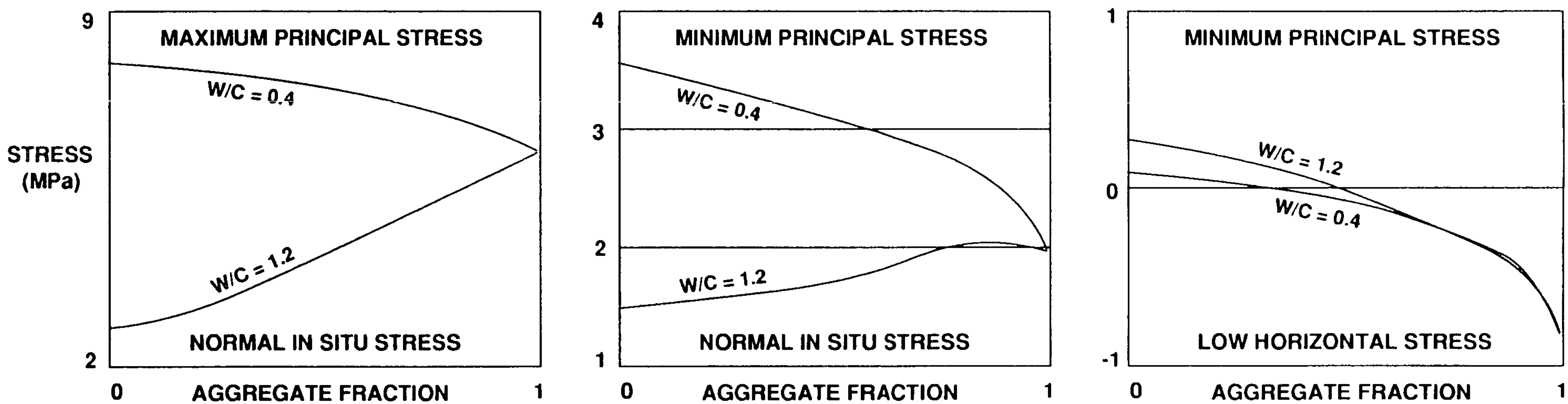
Overview

Cementitious Sealing Material Degradation Model



Mechanical Interactions

- **Minimum and maximum principal stresses--spherical inclusion** (Jaeger and Cook)

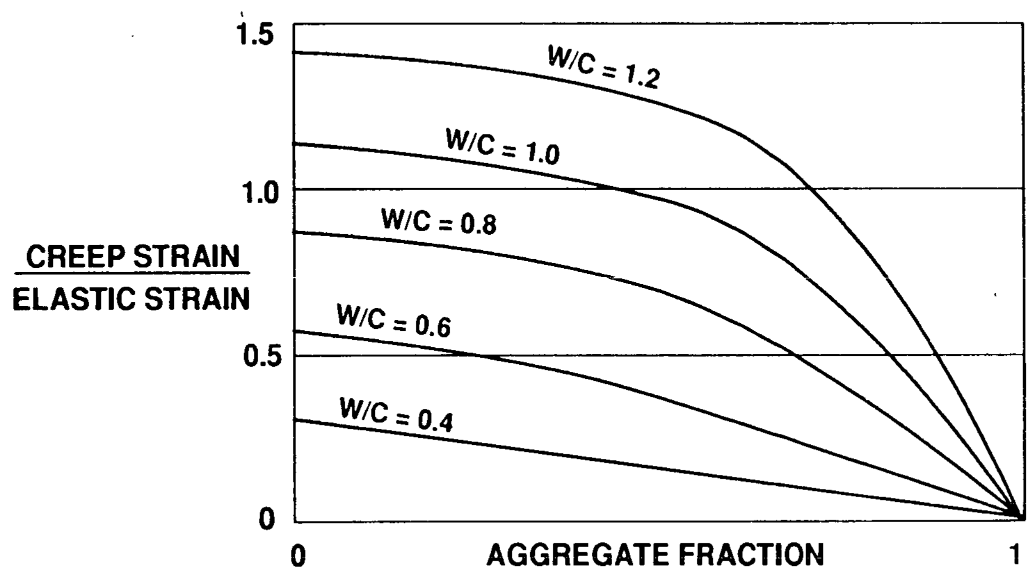


- **For normal in situ stresses--plug stresses are minor**

- **For low horizontal stresses--high water/cement ratios and low aggregate fractions are preferred**

Mechanical Interactions

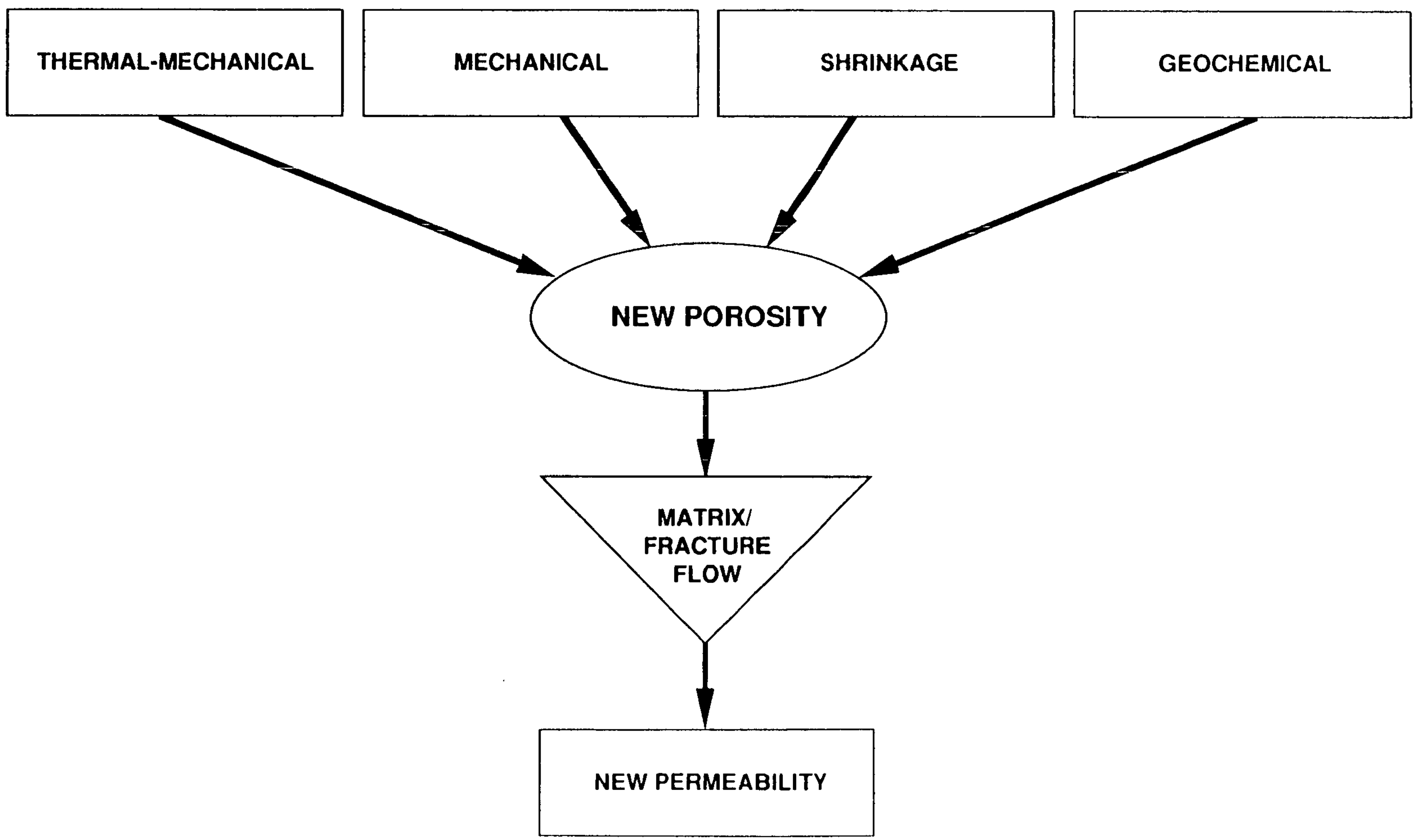
Creep



- Comité Européen du Beton method
- Creep increases with higher water-to-cement ratios
- Creep increases with lower aggregate fractions
- Higher water-to-cement ratios and lower aggregate fractions preferred

Overview

Cementitious Sealing Material Degradation Model



Shrinkage Interactions

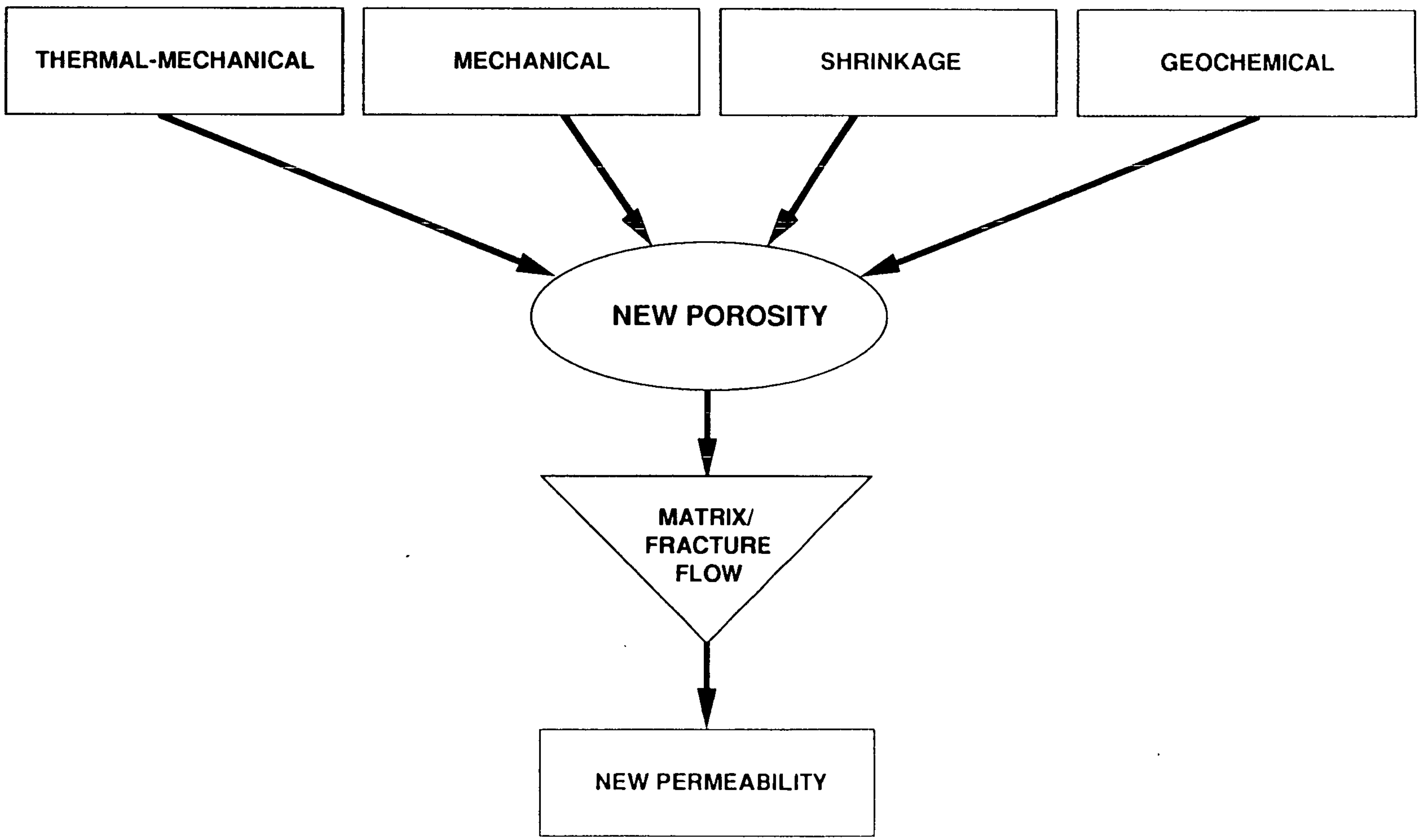
- Shrinkage-swelling effects controlled by relative humidity variations
- For in situ saturations between 0.4 and 1.0, the relative humidity is bounded between 0.97 and 1.0

Conclusion

- Saturation variation will have little effect on shrinkage-swelling effects

Overview

Cementitious Sealing Material Degradation Model



Geochemical Interactions

- Cement - J-13 water interactions

Future Considerations

- Cement-tuff-water interactions
- Kinetic effects
- Leaching effects
- Validation

EQ3NR/EQ6 Geochemical Code Assumptions for the Interaction of Concretes with J-13 Water

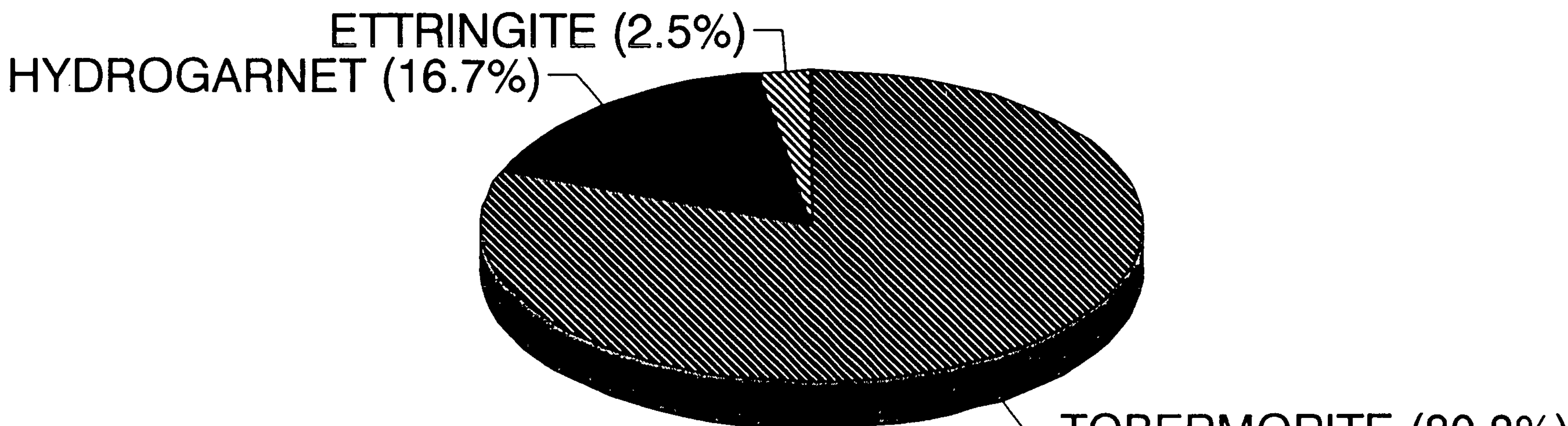
- Use of surrogates

BASE MATERIAL	SURROGATE
C-S-H GEL	TOBERMORITE
C_3AH_6	HYDROGARNET
SULPHATE CEMENT PHASE	ETTRINGITE
SiO_2	CRISTOBALITE

- Local equilibrium assumed
- Closed system assumed--dissolved gases limited
- Minerals suppressed

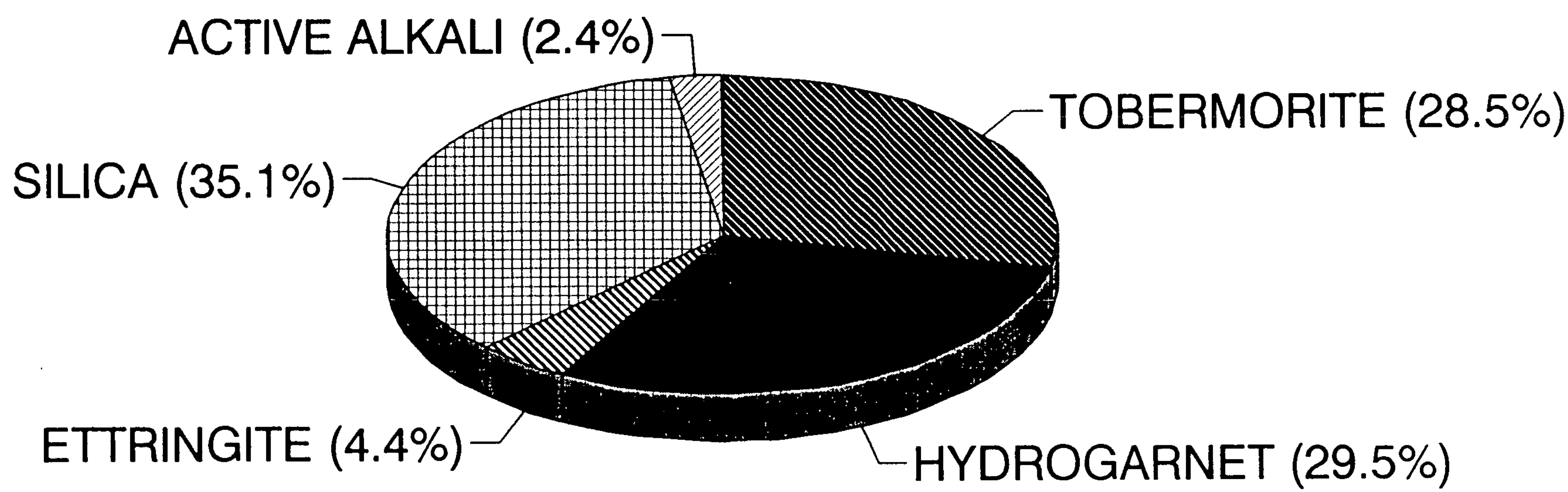
OPC-B Concrete

OPC with Balanced Silica and Calcium



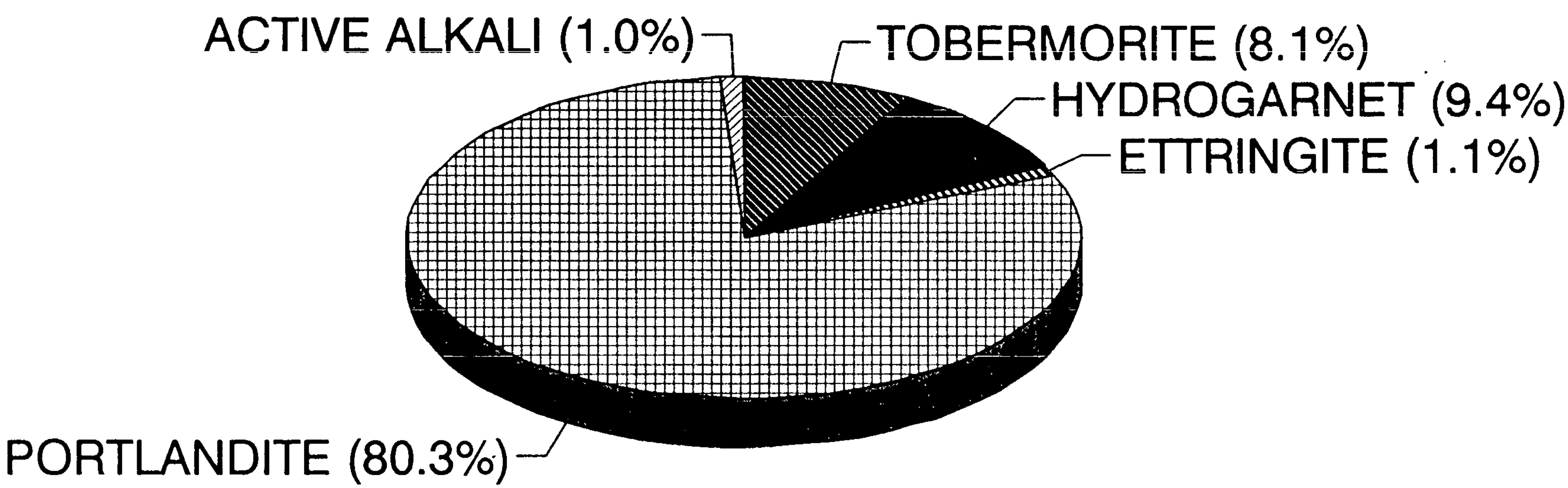
EPC-S Concrete

Silica-Rich, Ettringite-Rich Concrete



OPC-C Concrete

Calcium-Rich, OPC Concrete

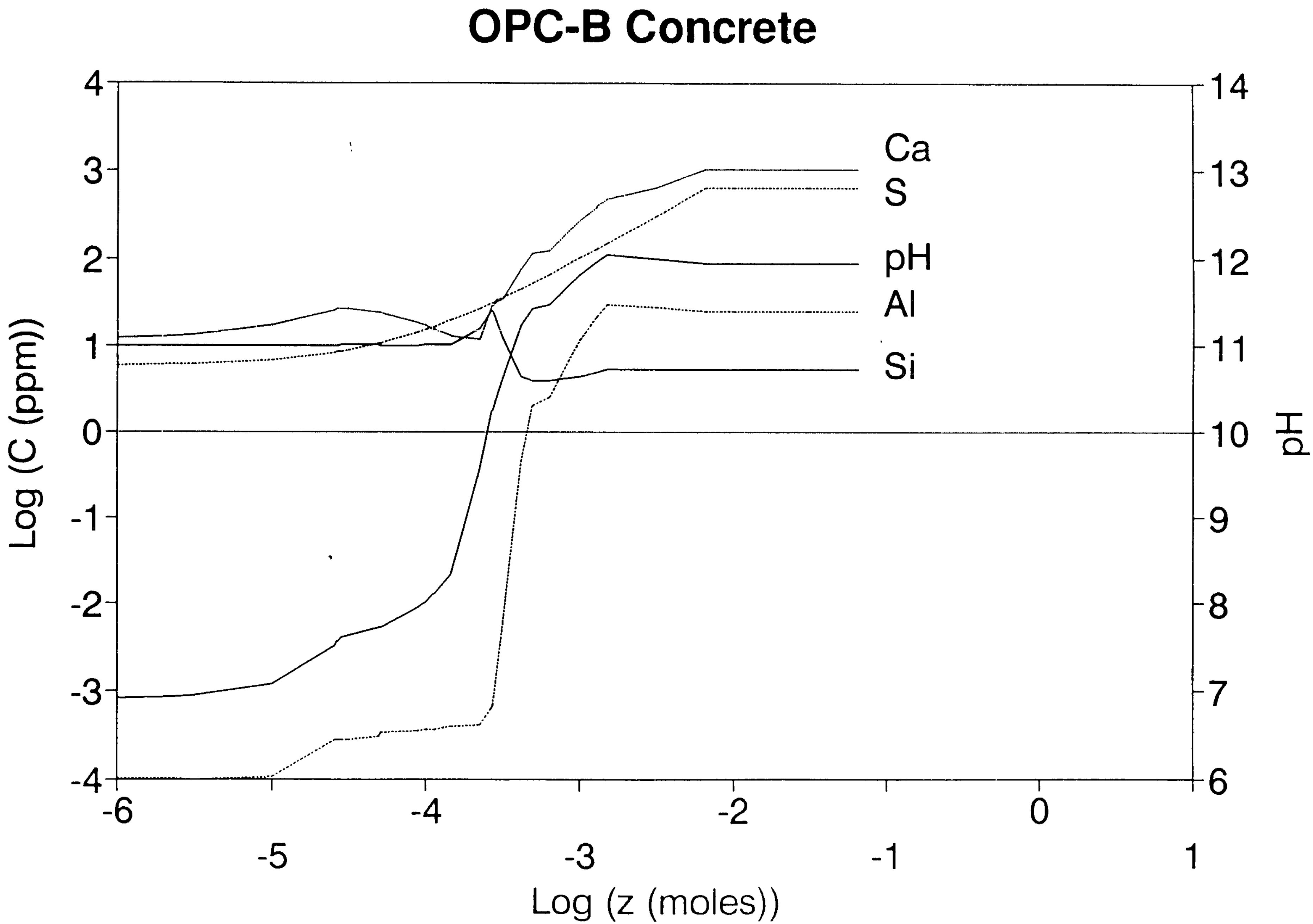


J-13 Water Composition

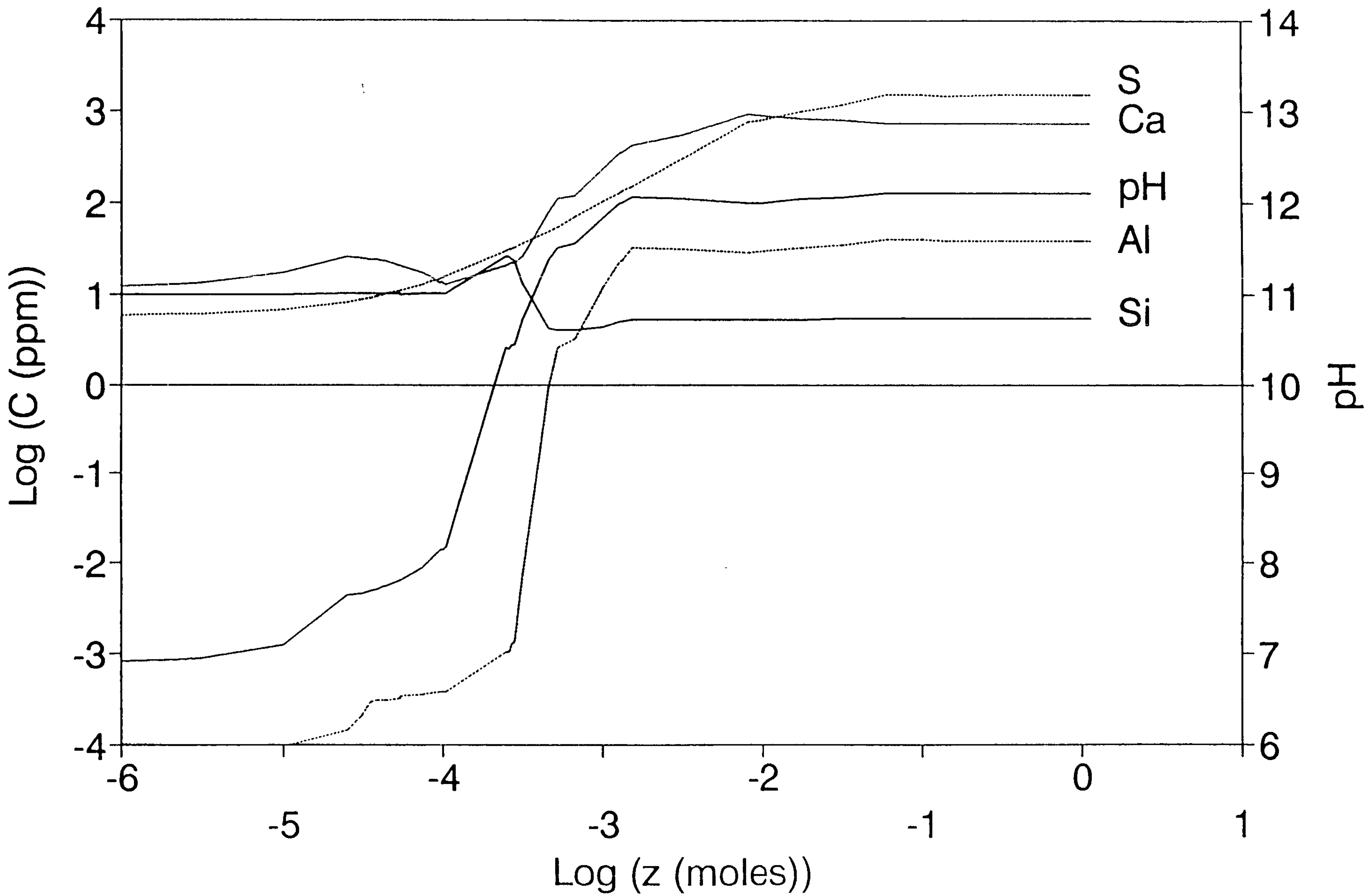
SPECIES	CONCENTRATION (mg/L)
Ca	11.62
Mg	1.75
Na	45.1
K	5.32
Li	0.062
Fe	0.045
Mn	0.001
Al	0.027
Si	30.05
F^-	2.1
Cl^-	6.4
SO_4^{-2}	18.25
NO_3^-	9.92
HCO_3^-	142.8[(1)]

pH	6.9
Eh	0.120 V

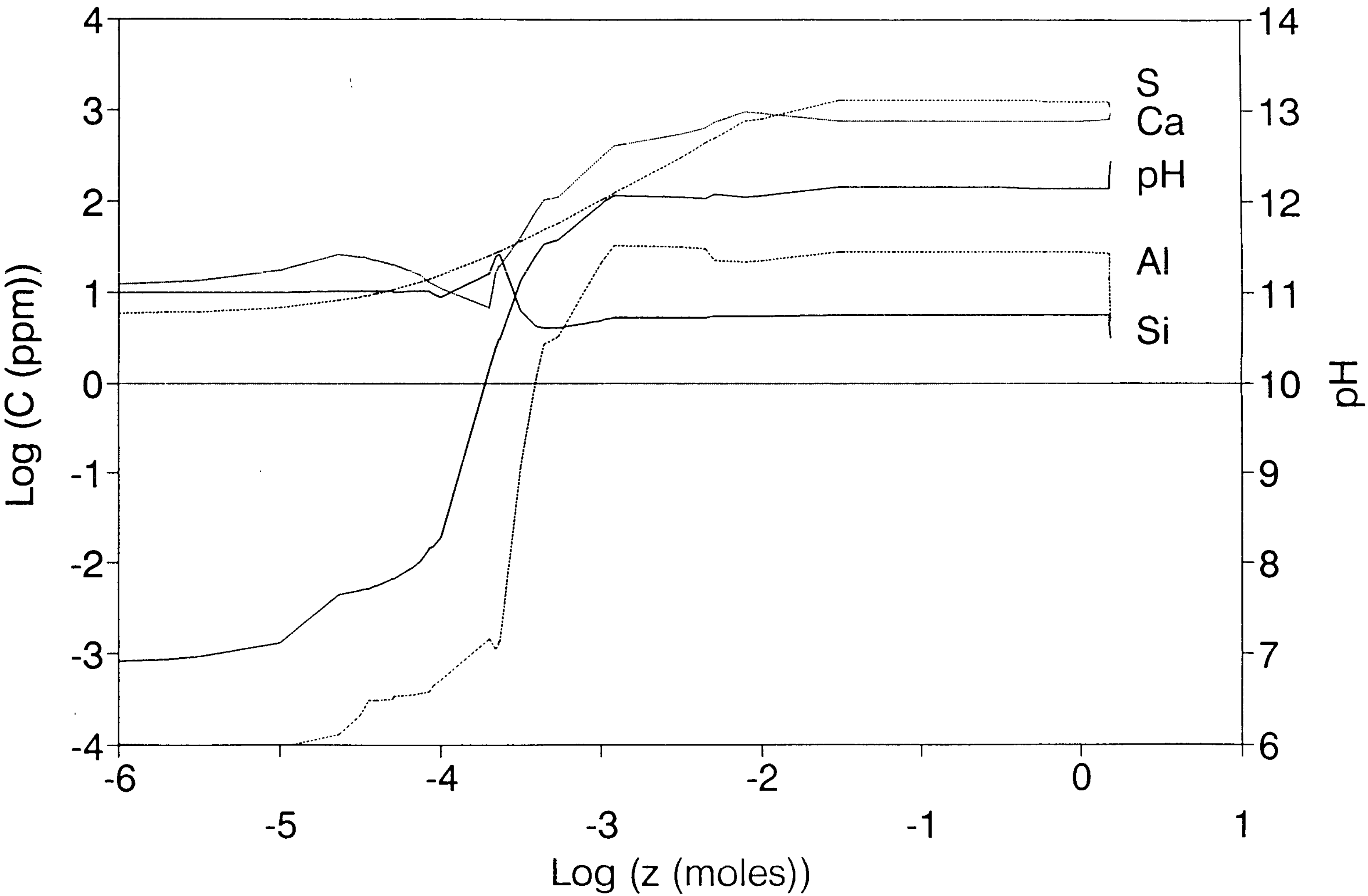
1. Titration alkalinity expressed as HCO^{3-}.


OPC-B Concrete
Ca
S
pH
Al
Si
Log (C (ppm))
pH
Log (z (moles))
4
3
2
1
0
-1
-2
-3
-4
14
13
12
11
10
9
8
7
6
-6
-4
-2
0
-5
-3
-1
1

EPC-S Concrete

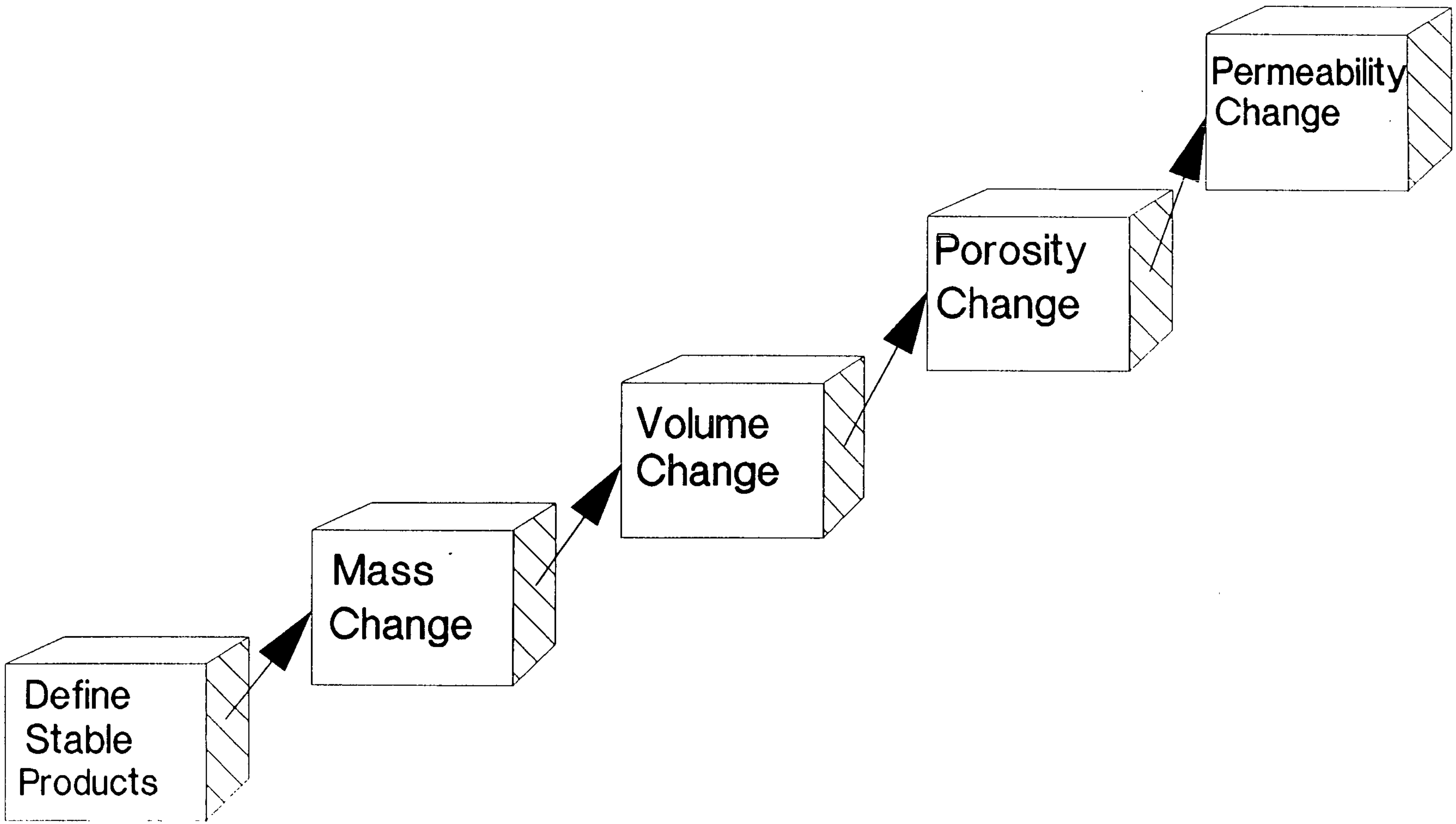


OPC-C Concrete

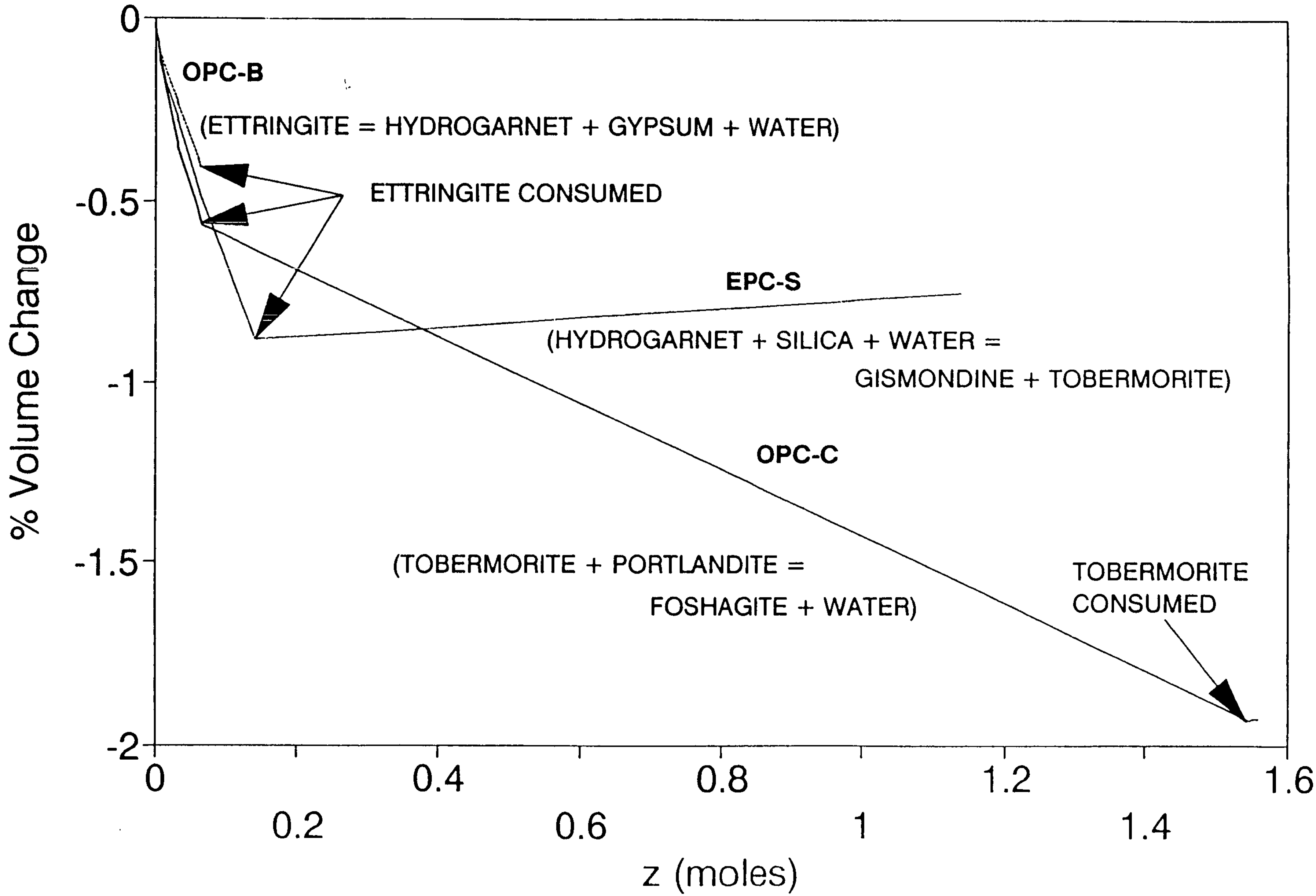


Steps in Modeling Cement

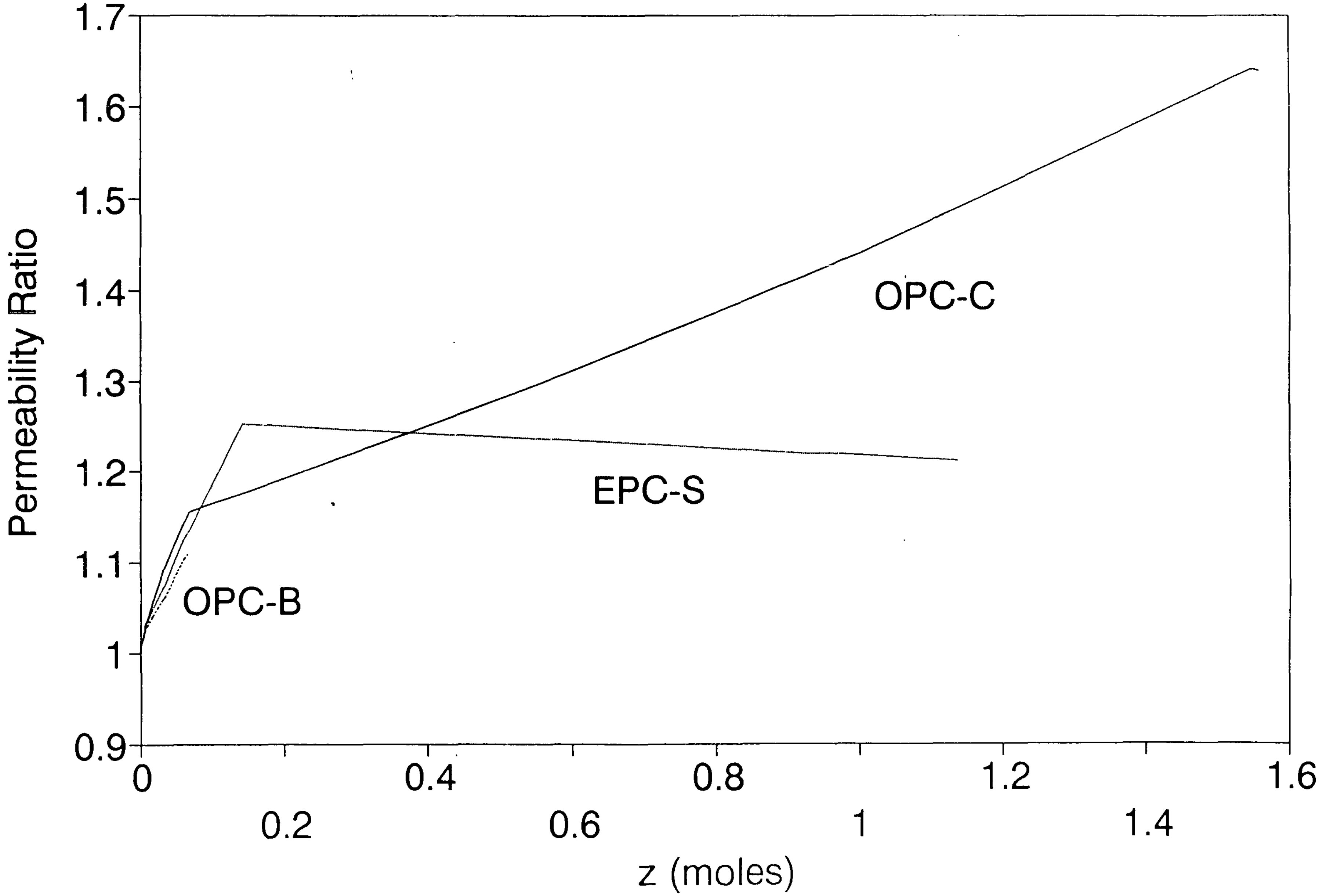
Permeability Modification



Projected Change in Volume



Projected Change in Permeability



Summary of Geochemical Interactions

Water Chemistry

- Calcium-rich and silica-rich concretes have similar responses in J-13 water
  - Small concrete addition--solution strongly buffered by J-13 water
  - Large concrete addition--concrete dominates solution

Concrete Alteration

- For closed system--reducing conditions and minimal carbonate formation
- Mass and volume change is described by a few chemical reactions
  - Ettringite and Portlandite open concrete structure
  - Excess silica tightens the concrete structure
- Permeability changes for this study are small

Conclusions from Geochemical Considerations

- Material screens indicate that both cements and earthen materials are potentially suitable as sealing materials
- Cementitious material evaluations indicate that high-quality cementitious sealing materials may be achievable by controlling the cement composition
  - Important factors
    - Calcium-to-silica ratio
    - Water-to-cement ratio
    - Aggregate weight percent
    - Gypsum
    - Portlandite
    - Unreacted cement phases