

# TECHNISCHER BERICHT 82-03

The Long-Term Stability of Cement  
and Concrete for Nuclear Waste Disposal  
under Normal Geologic Conditions

Woo Seung Shin

March 1982

BATTELLE, Geneva Research Centres



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### Summary

The nuclear power industry which has developed in this century has raised new and interesting issues in the management and disposal of radioactive waste materials. The treatment and disposal of radioactive waste involve both environmental considerations and technical processing problems. The increasing emphasis upon environmental considerations as they relate to nuclear wastes has focused additional attention upon the long-term stability of cement and concrete for nuclear waste disposal under potential geologic repository conditions.

Brief descriptions of scientific background to cement and concrete, and discussions related to the stability of structure, corrosion of reinforcement, possible environmental conditions in a potential repository site in Switzerland, and the influence of environment on cement and concrete are presented. More emphasis is placed on the thermal and pressure environment, and the effect of groundwater in a reducing environment.

The cement compositions for the immobilization of radioactive wastes are briefly commented upon from the standpoint of the cementing mechanism for compatibility with radioactive wastes, leachability, and chemical and mechanical durability.

Long-term stability of concrete based on chemical change, structural behaviour and mechanical integrity is considered during the period of 0-100 years and the period of  $10^2$ - $10^4$  years. Included are suggestions for future work, which would provide vital information for predicting more accurately the long-term behaviour of cement and concrete used in the repository environment.

The following conclusions of this review provide a basis for general considerations on the selection of cement and concrete for nuclear waste disposal:

- Cement should be of a sulphate-resisting and low-heat type with a relatively high C<sub>2</sub>S content. This will reduce the risk for thermally-induced cracks during construction. The long-term durability and strength tend also to be higher for this type of cement.
- The aggregate with high strength and low permeability must not contain minerals which react with cement paste and form detrimental products under high pressure and temperature.
- The water-cement ratio should preferably be as low as possible since it influences the gel-pore structure of the concrete and has a significant effect on the stability and durability of the concrete.
- The use of admixtures and additives should be avoided unless their effects on the long-term stability of cement and concrete are exactly known. Many additives have multiple effects and great care is required to select an optimum additive for specific application in repository site.
- The composition of concrete mix should be carefully selected for producing a dense, high quality concrete permitting a minimum of infiltration by groundwater and strict requirements must be established on the construction of concrete for maintaining its integrity for very long time periods.
- Cement can also be used for the solidification of low-level, intermediate-level and aged high-level radioactive wastes. Advantages of cement include inexpensive raw materials, low processing temperatures and process simplicity. Concrete waste forms show relatively acceptable thermal, chemical, physical and radiolytical stability.

## ZUSAMMENFASSUNG

Die in diesem Jahrhundert entwickelte nukleare Energieindustrie hat bezüglich Behandlung und Beseitigung von radioaktivem Abfall neue und interessante Fragen aufgeworfen. Insbesondere befasst man sich mit Problemen der Umwelt und der technischen Verarbeitung. Die zunehmende Bedeutung der Umweltaspekte hat in vermehrtem Masse die Aufmerksamkeit auf das Langzeitverhalten von Zement und Beton bei der Lagerung radioaktiver Abfälle unter möglichen geologischen Bedingungen gelenkt.

Eine kurze Beschreibung der wissenschaftlichen Grundlagen von Zement und Beton sowie Diskussionen betreffend die bautechnische Stabilität, Korrosion der Bewehrung, mögliche Bedingungen in einer potentiellen Lagerstätte in der Schweiz sowie der Einfluss dieser Umgebung auf Zement und Beton werden präsentiert. Besonders hervorgehoben werden die Auswirkungen aufgrund der Wärme- und Druckverhältnisse in tiefen Lagerstätten sowie der Effekt des Grundwassers in einer reduzierenden Umgebung.

Die Zementzusammensetzungen für die Konditionierung von radioaktivem Abfall sind kurz kommentiert hinsichtlich Verträglichkeit mit radioaktiven Abfällen, Auslaugung sowie chemischer und mechanischer Stabilität.

Die Langzeitstabilität von Beton, basierend auf chemischen Veränderungen, bautechnischem Verhalten und mechanischer Integrität ist für die Dauer von 0 - 100 Jahren sowie für die Dauer von  $10^2$  -  $10^4$  Jahren in Betracht gezogen worden. Es werden Vorschläge für weitere Abklärungen gegeben, die entscheidende Informationen hinsichtlich der genaueren Vorhersage des Langzeitverhaltens von Zement und Beton unter Lagerstättenbedingungen ermöglichen sollen.

Die nachstehenden Schlussfolgerungen geben eine Basis für generelle Betrachtungen bei der Wahl von Zement und Beton im Zusammenhang mit der Beseitigung des radioaktiven Abfalls:

- Der Zement sollte sulfatbeständig sein und einen relativ hohen Gehalt an  $C_2S$  sowie eine geringe Abbindewärme aufweisen. Dadurch wird das Risiko für wärmeinduzierte Spannungsrisse vermindert. Die Beständigkeit und Betonfestigkeit scheinen für diesen Zementtyp höher zu sein.
- Die Zuschlagstoffe mit hoher Festigkeit und geringer Durchlässigkeit sollten keine Mineralien enthalten, die mit dem Zement reagieren und sich unter hohem Druck und hoher Temperatur zersetzen.
- Das Wasser-Zement-Verhältnis sollte vorzugsweise so niedrig als möglich sein, weil es die Gel-Struktur des Betons beeinflusst und einen entscheidenden Einfluss auf die Stabilität und Beständigkeit des Betons ausübt.
- Der Gebrauch von Zement-Zusätzen sollte vermieden werden, es sei denn, ihre Auswirkungen auf die Langzeitstabilität von Zement und Beton seien genau bekannt. Viele Zusätze haben mehrere Auswirkungen und grosse Sorgfalt ist geboten bei der Wahl eines optimalen Zusatzes für eine spezifische Anwendung in einer Lagerstätte.
- Das Mischrezept für den Beton sollte sorgfältig ausgewählt werden, um einen dichten, qualitativ hochstehenden Beton zu erhalten, der für Grundwasser nur minimal infiltrierbar ist. Es müssen strenge Qualitätsanforderungen an die Verarbeitung des Betons gestellt werden, um die Langzeitstabilität zu erreichen.
- Der Zement kann auch für die Verfestigung von schwach-, mittelaktivem und abgekühltem hochaktiven Abfall verwendet werden. Die Vorteile von Zement sind niedrige Rohmaterialkosten, niedrige Verarbeitungstemperaturen und einfache Handhabung. In Beton verfestigte Abfälle zeigen relativ akzeptable thermische, chemische, physische und radiolytische Stabilität.

## Résumé

L'énergie nucléaire a soulevé de nouvelles et d'intéressantes questions quant à la gestion et à l'évacuation des déchets radioactifs. Le traitement et l'élimination de ces déchets impliquent à la fois des considérations d'environnement et des problèmes techniques de procédés. L'importance toujours plus grande donnée à l'environnement a mis en relief la stabilité à long terme du ciment et du béton dans les conditions prévalant dans un dépôt souterrain de ces déchets.

Une brève description des données scientifiques de base relatives au ciment et au béton est présentée. Elle est suivie d'une discussion de la stabilité structurelle de ces derniers, de la corrosion des parties de renforcement, des conditions pouvant régner dans un site de dépôt potentiel en Suisse et enfin de l'influence de ce milieu sur le ciment et le béton. L'accent a été placé sur les effets de température et de pression ainsi que sur ceux dus aux eaux souterraines en milieu réducteur.

Les compositions de ciment pour l'immobilisation des déchets radioactifs sont brièvement commentées du point de vue de la compatibilité du mécanisme de cimentation avec les déchets, de la lixiviation et de la résistance chimique et mécanique.

La stabilité à long terme du béton, quant à sa modification chimique, son comportement structurel et son intégrité mécanique, est considérée dans une première période de 0 à 100 ans et dans une deuxième période de 100 à 10'000 ans. Des suggestions sont faites pour un travail futur qui fournirait des informations essentielles pour une prédiction plus précise du comportement à long terme du ciment et du béton utilisés dans un dépôt.

Les conclusions suivantes qui en sont tirées forment une base de référence pour le choix du ciment et du béton destinés à l'isolation des déchets:

- Le ciment devrait être du type résistant au sulfate et à faible chaleur, avec un contenu relativement élevé en C<sub>2</sub>S. Ceci réduit le risque de fissure induite thermiquement pendant la prise. La résistance à long terme tend aussi à être plus élevée pour ce type de ciment.

- Un agrégat à haute résistance et faible perméabilité ne doit pas contenir des minéraux qui réagissent avec la préparation de ciment et qui forment des produits nuisibles à haute pression et température.
- Le rapport eau-ciment devrait être de préférence aussi bas que possible puisqu'il influence la structure en gel et pores du béton et par là de façon significative sa stabilité et sa résistance.
- L'utilisation d'additifs devrait être évitée à moins que l'effets de ces derniers sur la stabilité à long terme du ciment et du béton soient exactement connus. Beaucoup d'additifs donnent lieu à des effets multiples; une grande précaution est donc nécessaire lors du choix d'un additif pour une application particulière à un site de dépôt.
- La composition des produits de mélange devrait être soigneusement choisie afin de produire un béton dense et de haute qualité, minimisant l'infiltration d'eaux souterraines. Des exigences strictes sur la prise du béton sont à formuler pour maintenir son intégrité sur de très longues durées.
- Le ciment peut aussi être utilisé pour la solidification de déchets faiblement et moyennement radioactifs ainsi que pour celle de déchets hautement radioactifs s'ils sont agés. Les avantages du ciment sont d'être un matériau bon marché, à basse température de formation, et dont le procédé d'utilisation est simple. Les déchets conditionnés en béton montrent une stabilité thermique, chimique, physique et radiolytique relativement acceptable.

NOTATION

In designating cement and chemical compounds, a shortened notation is used where:

C : CaO

S : SiO<sub>2</sub>

A : Al<sub>2</sub>O<sub>3</sub>

F : Fe<sub>2</sub>O<sub>3</sub>

H : H<sub>2</sub>O

$\bar{C}$  : CO<sub>2</sub>

$\bar{S}$  : SO<sub>4</sub>

N : Na<sub>2</sub>O

M : MgO

AFm phase : monosulphate, [Ca<sub>2</sub>Al(OH)<sub>6</sub>]<sub>2</sub> (SO<sub>4</sub>) . 6H<sub>2</sub>O

Aft phase : [Ca<sub>3</sub>Al(OH)<sub>6</sub> . 12H<sub>2</sub>O]<sub>2</sub> (SO<sub>4</sub>)<sub>3</sub> . 2H<sub>2</sub>O

W/C ratio : water/cement ratio.

THE LONG-TERM STABILITY OF CEMENT AND CONCRETE  
FOR NUCLEAR WASTE DISPOSAL  
UNDER NORMAL GEOLOGIC CONDITIONS

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1. INTRODUCTION

Since the beginning of the nuclear industry thirty-five years ago, no final comprehensive plan has been established for the disposal of radioactive wastes from commercial nuclear power programs. A critical component of the important nuclear fuel cycle is the safe disposal of radioactive wastes.

Of the many disposal options which have been proposed for medium-level (MLW) and high-level wastes (HLW) three options appear to be feasible using current technology:

- emplacement in deep geologic formations on land
- emplacement on the bed of the deep ocean
- emplacement under the bed of the deep ocean.

One of the major factors in deciding whether disposal options are acceptable is the predicted radiological impact of disposal options [1-6]. Three major components in assessments of the potential radiological impacts of MLW and HLW disposal include:

- the mechanisms by which radioactivity may be released from the disposal site into the biosphere
- the probabilities of occurrence of the events and processes which could directly cause a release or could influence the rate at which the release occurs, and
- the evaluation of the radiological consequences of releases.

The research on disposal options can be divided into the following subject areas: waste form, waste package, engineered barriers and the disposal environment. The most complex of these, and the one to which most effort is devoted, is the disposal environment [7-10]. One of the most promising methods under study is underground disposal in deep geologic formations.

In a deep geologic repository for high level wastes physical and chemical conditions lead to an effective confining pressure of about 10 MPa, possible differential pressure up to 35 MPa, and temperatures up to around 100°C, and the likely presence of groundwater in a reducing environment. From the standpoint of both the waste isolation system and the long-term stability of cement and concrete used in the system, the thermal period of a geologic repository is the most critical. Heat production of HLW forms is dominated by the radioactive decay during the first several hundred years after closure of the repository. The repository contents and surroundings are likely to be subjected to the great thermal, mechanical and chemical changes analogous to natural geochemical processes.

The most credible scenario for rapid mobilization of the radionuclides contained in the waste form is intrusion of groundwater into the repository. If this occurs during the thermal period, then the combination of heat and pressure would create a hydrothermal environment that could accelerate corrosion and breaching of the canister and subsequent interactions of the hydrothermal solutions, the wastes, concrete, the host rock, the remains of the canister and any engineered containment structures.

It is well known that even the relatively low grade hydrothermal conditions possible in the HLW repository can cause extensive modifications in rocks and minerals. At the end of the thermal period the residues of the original waste plus the interaction products would constitute the actual HLW form subject to the low temperature leaching and migration processes.

Dissolution and transport of radionuclides by groundwater are the main threats to the effective isolation of radioactive wastes by burial in deep geologic formations.

There are two factors governing this transport:

- the rate of release of the radionuclides from the HLW solid and its engineered containment
- the rate of radionuclide migration through the various geologic formations between the repository and the biosphere.

To model the potential escape of radionuclides through the repository site geologic media should be considered as well as environmental parameters such as pressure, temperature and chemical conditions surrounding a repository (including anticipated changes both natural and man made). Important properties of geologic media include:

- Geologic:  
Lithology (rock type), stratigraphy (e.g. thickness, uniformity) and structure (e.g. folding, joints and faults)
- Hydrogeologic:  
Existence of aquifers and the directions of groundwater flow on a regional and local basis.
- Geochemical:
  - . the rate at which radionuclide movement is retarded relative to groundwater movement as a result of interactions with geologic materials
  - . how geologic materials will behave when internal and/or environmental conditions are changed
  - . reactions which may result from contact of HLW or other man-placed materials with the geologic media.
- Thermal:  
How the geologic media will behave under thermal stress (in particular, differential expansion); and the rate at which heat can be dissipated and interact with the radioactive waste or other man-placed materials.

- Engineering:

Local structural behaviour at the disposal opening (e.g. cavern, entry, shaft, borehole) before and after the opening is backfilled and, more importantly, how the media will respond to displacement changes due to large scale geologic events. Engineering properties pertinent to the underground nuclear waste disposal include:

- . permeability
- . strength
- . modulus of elasticity
- . chemical and physical stability
- . creep.

The major host rocks for the geologic repository are salt deposits (either bedded or in domed structures), hard crystalline igneous or metamorphic rocks (granites, gabbros, gneisses, granulites, etc.), and argillaceous rocks. All are chosen for their relative impermeability, large-scale homogeneity, and massive and widespread nature. Salt and some clay deposits have the advantage of being self-sealing; clays have a high ion-adsorption capacity which would impede any nuclide migration; and crystalline rocks can be identified which are generally dry, stable against geological movements both vertically and laterally, and insensitive to low quantities of heat. Eventual site investigation will obtain a structural, textural, chemical and hydrogeological picture of the rock volume to determine overall suitability and optimum position within the zone for a repository.

Cements and concretes have played a significant role in the solidification and disposal of low-level (LL) and medium-level (ML) commercial nuclear wastes as well as defence HLW for many years on an industrial scale. Cement has many favorable characteristics which make it an attractive candidate for a waste binding agent. It is widely available, inexpensive, non-combustible, radiation-resistant, and has good chemical, mechanical and thermal stability at the temperature reached with LL and ML wastes. Optimally processed cement/waste composites, which are made by low-temperature processes, using well established concrete technology, are relatively non-leachable and constitute durable waste forms.

The main thrust of current development effort concerned with LL and ML wastes is to define and demonstrate measures for their permanent safe disposal. The Deutsche Gesellschaft für Wiederaufarbeitung von Kernbrennstoffen GmbH (DWK) has recently decided upon the fixation of LL and ML liquid wastes by the cementation process permitting higher thermal loading after a thorough study of various cement/waste forms. Solid LL and ML wastes have been treated by adequate mechanical means such as compacting followed by the cement solidification process. At Oak ridge National Laboratory cementitious grout is used for the fixation and isolation of ML wastes by the hydrofracturing process in the Conasauga shale bed formation. The LL and ML waste/cement composites can be emplaced at a repository site deep in a hard-rock formation.

In current waste repository projects, cements or concretes may find several possible applications. Cementing applications may be divided into four types:

- matrix for the solidification of radioactive wastes
- structural application:  
to form concrete/rock wall structure along the shaft, gallery and cavern, and to protect the backfilling materials (e.g. bentonite) and sealing concrete
- filling application:  
to fill all the holes and interstitial space between canisters or between drums
- sealing application:  
to close the boreholes, shaft, tunnel, and entry and to prevent adverse interzonal migration of fluids. Each seal may consist of several components with predetermined functions corresponding to the basic 'multiple barrier' concept. The concept may incorporate a sorptive zone, one where any migrating fluid is exposed to materials which selectively retain undesirable materials, i.e. radionuclides. In this zone, the characteristics of the bond and of the intrinsic permeability of the material itself

should be considered so that any flow can be preferentially localized to the vicinity of or through the sorptive material.

To provide an effective long-term stability the concrete should possess at least the following properties:

- adequate durability
- sufficiently low permeability to preclude excessive movement of groundwater
- appropriate strength and other physical properties.

Long-term stability of concrete is the most significant, and simultaneously the largest unknown factor in its application in a nuclear waste repository. The main objective of this review is to provide a general overview of long-term stability of cement and concrete for nuclear waste disposal under normal geologic conditions. It is essential to understand chemical, mechanical and thermal stability under a wide variety of conditions including elevated pressure, temperature and groundwater for prediction of long-term behaviour and assessment of suitability for use in radioactive waste repository environment.

2. SCIENTIFIC BACKGROUND TO CEMENT AND CONCRETE2.1 CEMENT

The main chemical constituents of Portland cement [11] are the anhydrous compounds tricalcium silicate ( $C_3S$ ), dicalcium silicate ( $\beta$ - $C_2S$ ), tricalcium aluminate ( $C_3A$ ), and an aluminoferrite solid solution phase approximately corresponding to the formula  $C_4AF$  as can be seen in Table 1. All these compounds, in a finely powdered form, readily react with water giving insoluble hydration products which gradually replace the water in the spaces between the cement grains and eventually provide a matrix that effectively binds the cement mass together.

TABLE 1 - COMPOSITION OF SOME PORTLAND CEMENTS [ref. 11]

	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	TiO <sub>2</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	SO <sub>3</sub>	Free CaO	$C_4AF$	$C_3A$	$C_3S$	$C_2S$
Ordinary	65.6	0.70	4.31	2.55	23.73	0.24	0.31	0.66	1.00	1.0	8	7	47	32
	65.5	1.23	5.90	1.59	22.76	0.33	0.43	0.50	1.60	1.4	5	13	41	34
	64.4	0.89	5.36	3.27	21.19	0.34	0.36	0.58	2.53	1.9	10	9	45	27
	64.6	0.56	7.64	3.30	19.09	0.34	0.25	0.57	2.19	0.6	10	15	53	15
	65.5	0.97	6.85	2.30	20.54	0.35	0.16	0.76	1.54	2.0	7	14	48	22
	63.1	0.82	6.28	3.59	20.56	0.37	0.27	0.58	2.59	1.7	11	11	39	30
Rapid-hardening	64.5	1.28	5.19	2.91	20.66	0.30	0.08	0.70	2.66	2.0	9	9	50	21
	65.4	0.51	5.00	4.31	20.04	0.42	0.48	0.78	1.47	1.4	13	6	64	9
	63.0	1.46	6.07	2.67	20.21	0.33	0.12	0.94	2.10	1.5	8	12	46	23
	64.3	1.27	4.74	2.15	22.37	0.36	0.18	0.53	1.82	2.3	7	9	42	32
Sulphate-resisting	63.8	0.92	4.07	4.65	21.09	0.28	0.13	0.67	2.56	2.9	14	3	58	17
	64.5	0.89	3.13	5.23	22.14	0.21	0.18	0.45	2.08	1.5	16	0	54	22
Low-heat	61.8	1.69	4.60	2.07	25.08	0.25	0.19	0.77	2.57	0.7	6	9	17	59
	62.0	1.59	4.54	2.06	25.80	0.23	0.20	0.65	1.87	0.9	6	9	15	63

### 2.1.1 HYDRATION MECHANISM OF PORTLAND CEMENT

The hydration of Portland cement involves a two-stage process [12-15]. The reaction is proceeded by:

- the rapid formation of coatings of gelatinous hydration products around the cement grains which inhibit subsequent reaction during the 'dormant stage', and
- the eventual growth from these coatings of fibrillar C-S-H gel material which, by formation of a reticulate and interlocking network between the cement grains, is thought to be a significant factor in the development of strength of the cement paste.

The sequence of cement hydration [16] is illustrated diagrammatically in Fig. 1.

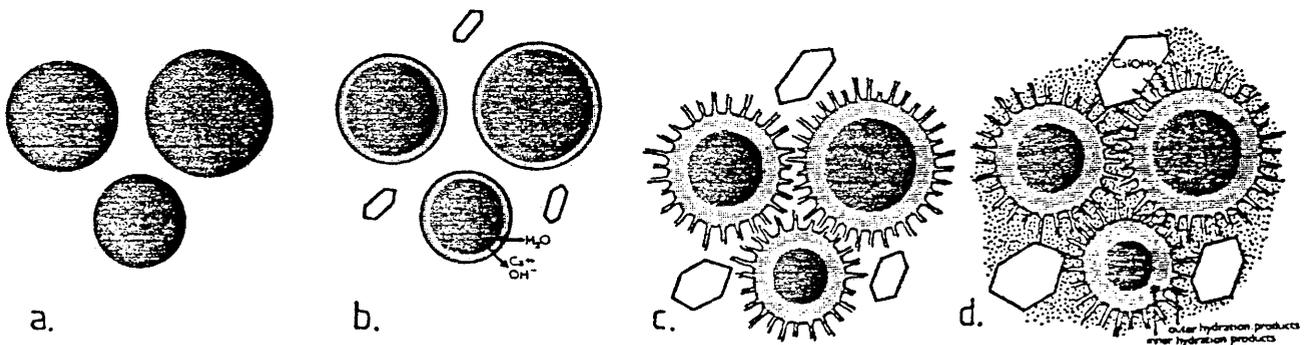


FIGURE 1 - DIAGRAMMATIC REPRESENTATION OF THE SEQUENCE OF HYDRATION OF CEMENT [Ref. 16]

- (a) Cement grains in water
- (b) Initial gel coatings around cement grains
- (c) Secondary growth of C-S-H gel after osmotic rupture of gel coatings
- (d) Long-term infilling and consolidation of microstructure.

In the early stages of hydration preferential diffusion through the membrane coating leads to the development of an osmotic pressure within membrane coating around the cement grains. Because of osmotic pressure effects [17] the gel coatings around the cement grains rupture and hydro-silicate material is extruded through the ruptured membrane and combines with the calcium ions in solution to precipitate C-S-H gel as excrescences on the surfaces of the cement grains. A diffusion-controlled phase reaction proceeding by nucleation and growth and precipitation processes [16,18] become more important in the progressive infilling and consolidation of the cement microstructure.

### 2.1.2 STRUCTURE OF CEMENT PASTE

In a hardened cement paste [19-21] the C-S-H gel, in a finely divided and largely amorphous form, occupies about 70% of the hydrated material and thus forms the main bonding agent between the residual grains of cement and other crystalline products of hydration. The cement paste hydrated at normal temperatures also contains about 20% of well-crystallized  $\text{Ca(OH)}_2$ , and small percentages of ettringite,  $\text{C}_4\text{A}\bar{\text{S}}\text{H}_{12}$ , an AFm (hexagonal plate) or an AFt (ettringite-type) phase and several minor substances.

C-S-H gel has a variable composition with typically a high C/S mole ratio ranging between 2 and 3 and extensive incorporation of  $\bar{\text{S}}$ , Al and Fe ions and likely small amounts of K, Na and other ions as well. A classification [22] of at least four morphologically distinct varieties of C-S-H gel includes Type I-fibrous particles, Type II-reticular network, Type III-small grains of similar dimensions, and Type IV-inner product.

### 2.1.3 PHYSICAL AND STRENGTH PROPERTIES

The manner of filling of the original water-filled spaces with hydration products in the cement paste depends upon the particle size distribution of the cement, the water-cement ratio and the availability of water during hydration. The bulk density of Portland Cement hydration products [23] is tabulated with total pore volume, degree of hydration and permeability in Table 2.

TABLE 2 - CHARACTERISTICS OF CEMENT PASTE MADE WITH VARYING WATER-CEMENT RATIO [Ref. 23]

Water-cement ratio	Age	Bulk density g/cc	Total pore volume cc/g	Degree of hydration %	Permeability $\times 10^{-11}$ cm/sec
0.3	28 days	1.89	n.a.	54.59	1
	90 days	1.88	0.147	57.34	0.6
	1 year	1.94	0.130	64.68	0.4
0.4	28 days	1.65	n.a.	61.93	2.0
	90 days	1.70	0.196	64.68	1.0
	1 year	1.75	0.164	71.56	1.0
0.5	28 days	1.50	0.295	64.22	3
	90 days	1.57	0.253	71.10	3
	1 year	1.57	0.247	75.23	1
0.6	28 days	1.26	0.417	64.22	23
	90 days	1.33	0.368	73.85	3
	1 year	1.33	0.362	77.06	2
0.7	28 days	1.13	0.470	64.22	220
	90 days	1.24	0.414	75.23	18
	1 year	1.24	0.409	79.82	14
0.8	28 days	1.09	0.531	65.14	963
	90 days	1.12	0.501	75.23	77
	1 year	1.12	0.503	79.82	45
0.9	28 days	0.91	0.713	66.06	4 100
	90 days	0.99	0.622	75.23	175
	1 year	0.99	0.619	79.82	76

n.a. = not available

Pore size distributions of natural cement pastes and cement pastes hydrated for various ages are shown in Fig. 2 and Fig. 3, respectively. Studies of the pore size distributions of hardened cement paste [24,25,26] generally indicate the existence of a threshold diameter, which corresponds to the 'minimum geometrically continuous' pore size in hardened cement paste.

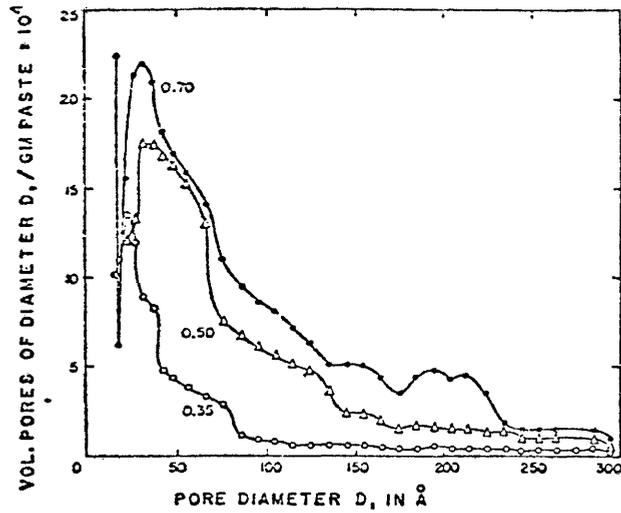


FIGURE 2 - PORE SIZE DISTRIBUTION OF MATURE CEMENT PASTES OBTAINED FROM NITROGEN ABSORPTION [Ref. 24]

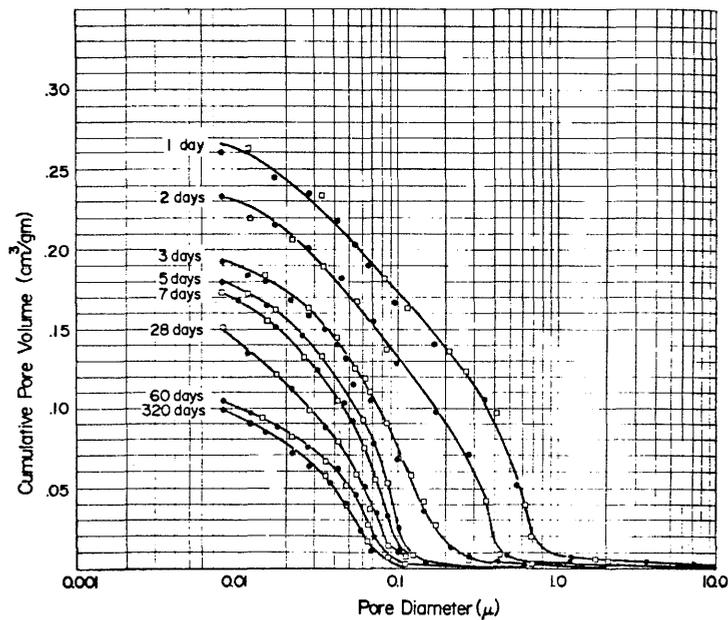


FIGURE 3 - PORE SIZE DISTRIBUTION OF CEMENT PASTES OF 0.4 WATER-CEMENT RATIO HYDRATED FOR VARIOUS AGES [Ref 25]

The beneficial effect of a reduction of water-cement ratio on the strengths of hardened cement paste [27] is usually attributed to the simultaneous decrease of their total porosity, as shown in Fig. 4. The strength of hardened cement paste at any time of its hardening is, in general, a power function of the volume occupied by the binding hydration products in a volume unit of hardened paste. Porosity is by far the most dominant controlling factor limiting the mechanical strength.

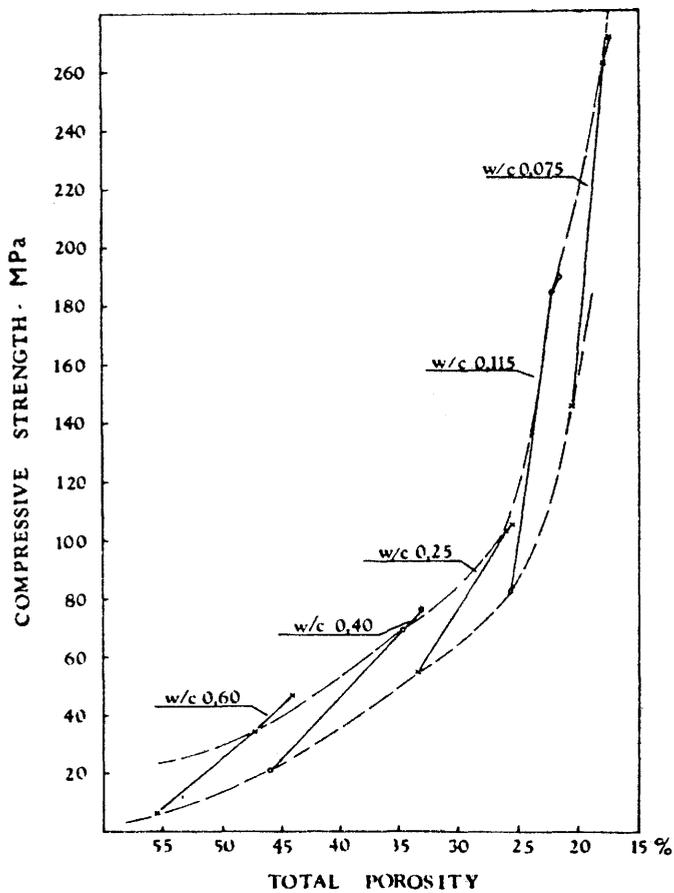


FIGURE 4 - RELATIONSHIP BETWEEN COMPRESSIVE STRENGTH AND TOTAL POROSITY OF HARDENED CEMENT PASTES WITH DIFFERENT WATER-CEMENT RATIOS [Ref. 27]

The permeability of hardened cement paste is mainly dependent on the capillary pore volume (Fig. 5). The relationship between permeability and total porosity [24,28] was found to satisfy the following equation:

$$K_1 = \frac{1.36 \times 10^{-10}}{\eta(T)} \frac{\varepsilon^2}{1 - \varepsilon} \exp \left[ - \left( \frac{1242}{T} + 0.7 \right) \frac{1 - \varepsilon}{\varepsilon} \right]$$

in which  $K_1$  is the permeability coefficient,  $\eta(T)$  is the viscosity of water in poises at temperature  $T(^{\circ}K)$ , and  $\varepsilon$  is the total porosity. The equation applies over the whole range, from fresh, plastic pastes, to mature pastes, as shown in Fig. 6.

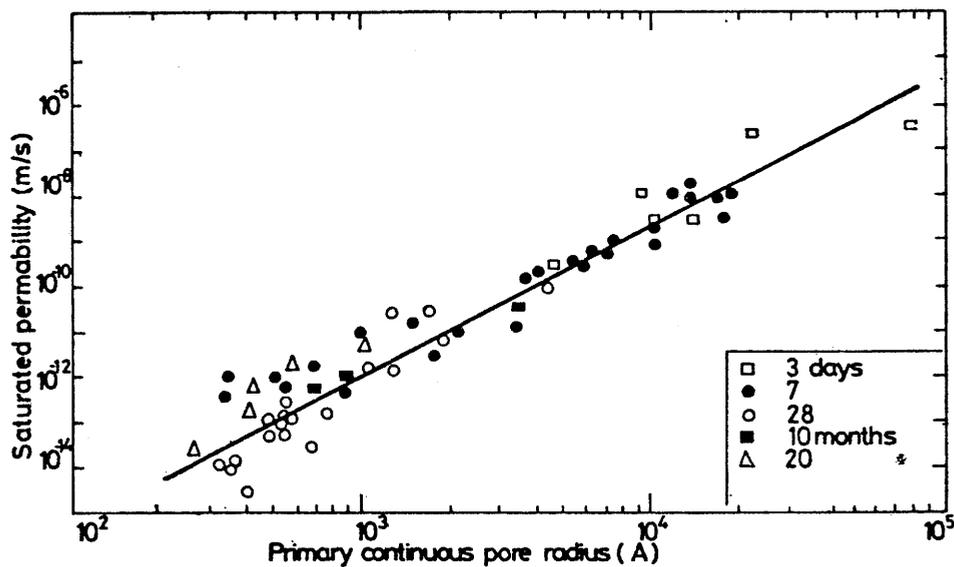


FIGURE 5 - RELATIONSHIP BETWEEN THE MAXIMUM CONTINUOUS PORE RADIUS AND SATURATED PERMEABILITY OF HARDENED CEMENT PASTE [Ref. 24]

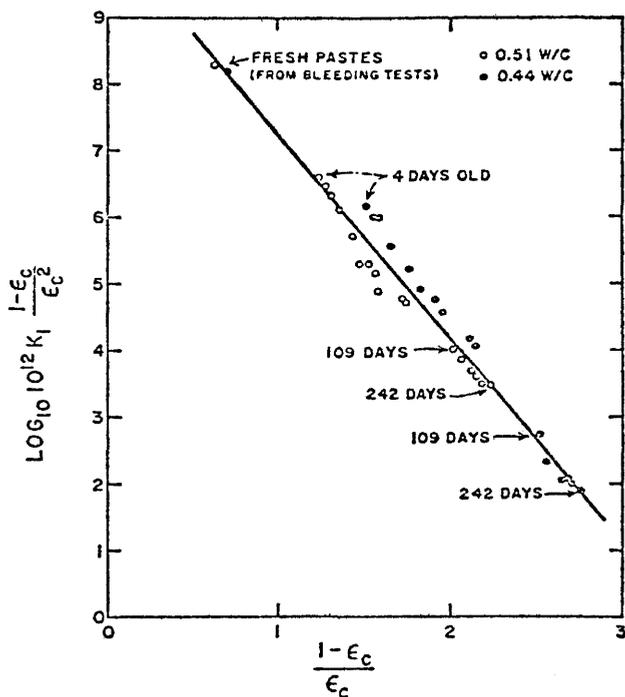


FIGURE 6 - THE FUNCTIONAL RELATIONSHIP BETWEEN PERMEABILITY AND CAPILLARY POROSITY IS LINEAR OVER THE POROSITY RANGE FROM FRESH PASTES TO ESSENTIALLY FULLY HYDRATED PASTES [Ref. 28].

## 2.2 AGGREGATES

Dense aggregates consists of natural sands, gravels, and crushed rocks, together with artificial products such as air-cooled blast furnace slag and broken brick. The nomenclature, mineral constituents, general classification and grading requirements of aggregates according to rock type are described in the national standards and specifications such as BS 812: 1967 and BS 883: 1965.

Specific gravities, porosity and compressive strength of rocks commonly used as concrete aggregates [29] are given in Tables 3, 4 and 5, respectively. All these properties have a considerable influence on the quality of the concrete either fresh or in the hardened state. The required strength of aggregate is considerably higher than the normal range of concrete strengths because the actual stresses at the points of contact of individual particles within the concrete may be far in excess of the normal compressive stress applied.

Table 6 gives the source and description of the rock samples. Data on the permeabilities of various rocks [30] are given in the first four columns of Table 7. The fifth and sixth columns give the water-cement ratios of mature pastes that would have the same coefficients of permeability as the corresponding rock samples.

Aggregates confer considerable technical advantages on concrete, which have a higher volume stability and better durability than the cement paste alone.

TABLE 3 - APPARENT SPECIFIC GRAVITIES OF DIFFERENT ROCK GROUPS [Ref. 29]

Rock group	Average specific gravity	Range of specific gravities
Basalt	2.80	2.6-3.0
Flint	2.54	2.4-2.6
Granite	2.69	2.6-3.0
Gritstone	2.69	2.6-2.9
Hornfels	2.82	2.7-3.0
Limestone	2.66	2.5-2.8
Porphyry	2.73	2.6-2.9
Quartzite	2.62	2.6-2.7

TABLE 4 - POROSITY OF SOME COMMON ROCKS [Ref. 29]

Rock group	Porosity, per cent
Gritstone	0.0-48.0
Quartzite	1.9-15.1
Limestone	0.0-37.6
Granite	0.4-3.8

TABLE 5 - COMPRESSIVE STRENGTH OF ROCKS COMMONLY USED AS CONCRETE AGGREGATES [Ref. 29]

Type of rock	Number of samples*	Compressive strength					
		Average †		After deletion of extremes‡			
		MN/m <sup>2</sup>	lb/in <sup>2</sup>	Maximum MN/m <sup>2</sup>	lb/in <sup>2</sup>	Minimum MN/m <sup>2</sup>	lb/in <sup>2</sup>
Granite	278	181	26,200	257	37,300	114	16,600
Felsite	12	324	47,000	526	76,300	120	17,400
Trap	59	283	41,100	377	54,700	201	29,200
Limestone	241	159	23,000	241	34,900	93	13,500
Sandstone	79	131	19,000	240	34,800	44	6,400
Marble	34	117	16,900	244	35,400	51	7,400
Quartzite	26	252	36,500	423	61,300	124	18,000
Gneiss	36	147	21,300	235	34,100	94	13,600
Schist	31	170	24,600	297	43,100	91	13,200

\* For most samples, the compressive strength is an average of 3 to 15 specimens. † Average of all samples. ‡ 10 per cent of all samples tested with highest or lowest values have been deleted as not typical of the material.

TABLE 6 - DESCRIPTION OF ROCK SAMPLES [Ref. 30]

Sample No	Lot No	Source	Description
4	18278	Eau Claire, Wis.	Trap rock, dense, some crystal-boundary pores
6	18393A	C.H. Scholer	Marble, fine grained, dense
2	-	Phillips, Wis.	Quartz diorite, coarsely crystalline, crystal-boundary pores
3	18278	Eau Claire, Wis.	Quartz-feldspar, felsite, very dense
9	-	Thomaston, Me.	Limestone, crystalline
11	-	Elmhurst, Ill.	Limestone, crystalline; fine-grained marble
12	-	Elmhurst, Ill.	Limestone, crystalline; fine-grained marble
5	18278	Eau Claire, Wis.	Quartzite, imperfectly cemented; sandstone
1	-	Elgin, Ill	Limestone, uniform, fairly dense, pure
8	18160	Santeetlah Dam	Granite, gray
7	18162	Baleigh County, W.Va.	Sandstone, porous
10	18200	Lithonia, Ga.	Granite

TABLE 7 - PERMEABILITY OF ROCKS COMPARED WITH THAT OF HARDENED PASTE [Ref. 30]

Sample No.	Density, g per cc	Evaporable water capacity, g per cc of sample	K <sub>1</sub> , cm per sec	Mature paste of same permeability, W/C		Evaporable water capacity, g per cc of paste
				by weight	gal. per sack	
4	2.99	0.0057	$3.45 \times 10^{-12}$	0.38	4.3	0.30
6	2.70	0.0052	$9.20 \times 10^{-13}$	0.41	4.6	0.34
2	2.94	0.0065	$1.15 \times 10^{-12}$	0.42	4.7	0.35
3	2.65	0.0018	$1.26 \times 10^{-12}$	0.42	4.7	0.35
9	2.71	0.0046	$1.72 \times 10^{-12}$	0.44	5.0	0.36
11	2.78	0.0180	$3.34 \times 10^{-12}$	0.48	5.4	0.39
12	2.75	0.0310	$8.05 \times 10^{-11}$	0.66	7.4	0.510
5	2.60	0.0140	$1.15 \times 10^{-10}$	0.68	7.7	0.515
1	2.72	0.0510	$2.30 \times 10^{-10}$	0.69	7.8	0.522
8	2.69	0.0073	$7.48 \times 10^{-10}$	0.70	7.9	0.529
7	2.58	0.0430	$1.72 \times 10^{-9}$	0.71	8.0	0.531
10	2.60	0.0052	$2.18 \times 10^{-9}$	0.71	8.0	0.532

## 2.3 CONCRETE

Concrete is one of the most versatile construction materials since its ingredients and proportions can be selected to produce the required properties for a given application and it can easily be cast into any desired shape. There are two overall criteria for good concrete: the concrete has to be satisfactory in its hardened state, and also in its fresh state while being transported from the mixer and placed in the formwork.

The requirements in the fresh state of the concrete are that the constitution of the mix be such that it can be compacted by standard means and also that the mix be cohesive enough for placing methods so that no segregation occurs causing a lack of homogeneity of the finished product. The usual primary requirement in hardened state of the concrete is a satisfactory mechanical strength, which ensures that the concrete can not only withstand a predetermined stress but also have other desired properties such as durability, impermeability and resistance to chemical attack, etc.

### 2.3.1 THE BOND BETWEEN CEMENTS AND AGGREGATES

The cement-aggregate bond results from some combination of mechanical interlocking provided by epitaxial growth of cement hydration products on the aggregate surface and chemical reactions between the cement paste and the aggregate. The contact zone between cement matrix and aggregate plays an important role in the development of the mechanical strength, especially of the very high strength concrete [31-35].

Bond strength varies widely according to the rock type and surface roughness of the aggregate and the tensile strength of the cement-aggregate bond is lower than that of the cement paste. Because the strength of the cement-aggregate bond is less than the strength of either paste or aggregate (Fig. 7), the bond would seem to be the weak link in the development of the strength of concrete [36].

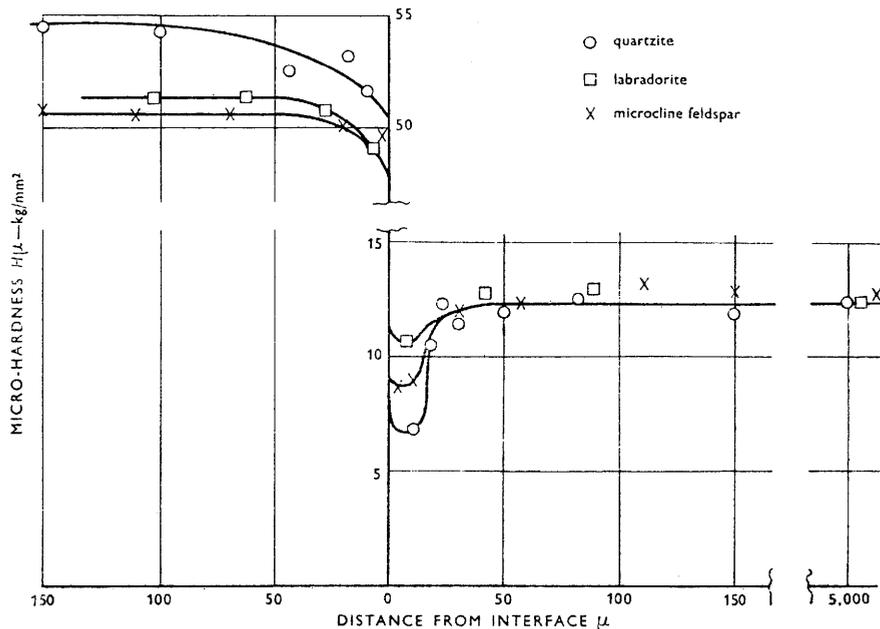


FIGURE 7 - VARIATIONS IN MICRO-HARDNESS ACROSS THE AGGREGATE-CEMENT INTERFACE [Ref. 36]

Fig. 8 shows reasonable correlation between bond strength and the compressive strength of the paste at 28 days and Fig. 9 covers the results of long-term test showing the effect of age on the bond and paste strength. After point A is reached, the mode of tensile fracture changes from preferential bond rupture to preferential failure in the paste [37]. Scholer [38] assumes that by observing microcracking in concrete during compressive strength measurements the cement-aggregate bond influences concrete failure. Studies [39] have been made of the degree to which the bond influences concrete strength and performance and it is suggested that a reduction in the incidence of bond cracks would decrease the permeability and, hence, improve the durability of concrete.

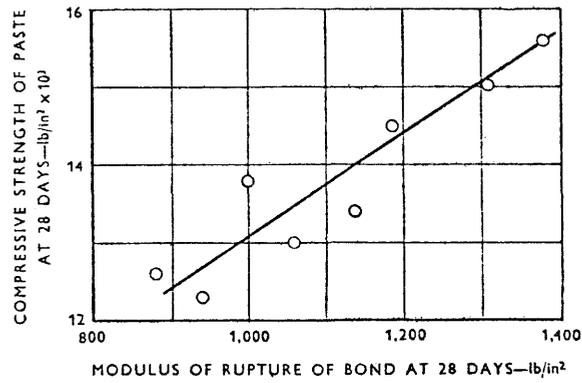


FIGURE 8 - RELATIONSHIP BETWEEN BOND STRENGTH AND PASTE STRENGTH FOR EIGHT BRANDS OF ORDINARY PORTLAND CEMENT AT A WATER-CEMENT RATIO OF 0.35 [Ref. 37]

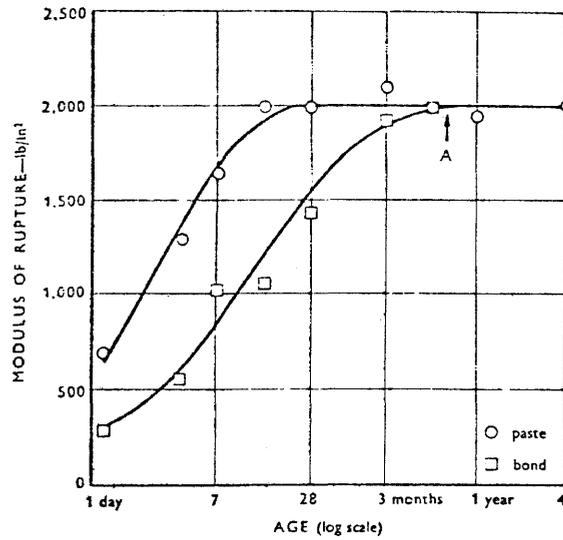


FIGURE 9 - LONG-TERM TEST SHOWING THE EFFECT OF AGE ON BOND AND PASTE STRENGTH (WATER-CEMENT RATIO 0.35) [Ref. 37]

### 2.3.2 PROPERTIES OF CONCRETE

Prediction of the over-all properties of a composite concrete system requires a knowledge of the volume fractions and properties of the constituents, as well as of the mechanism of interaction and whether mechanical, physical or chemical factors are involved between the separate phases. The various factors [40] which influence the intrinsic behaviour of concrete are listed in Table 8.

TABLE 8 - FACTORS AFFECTING THE INTRINSIC PROPERTIES OF CONCRETE SYSTEMS [Ref. 40]

---

<b>DEGREE OF HETEROGENEITY</b>	
Volume fractions of aggregate and paste. Maximum aggregate size and particle size distribution.	
<hr/>	
<b>PROPERTIES OF CEMENT PASTE</b>	
<i>Structure</i>	Volume fractions of unhydrated cement, cement gel, air and water voids. (Or degree of hydration or maturity in terms of age, type and pattern of curing, moisture content, temperature.)
<i>Mechanical</i>	Modulus of elasticity. Poisson's ratio. Inelastic or creep behaviour. Tensile and shear strengths; adhesive and cohesive strengths.
<i>Physical</i>	Volumetric stability. Shrinkage and swelling. Thermal movement. Porosity. Bulk density.
<i>Chemical</i>	Chemical composition.
<hr/>	
<b>PROPERTIES OF AGGREGATE</b>	
<i>Mechanical</i>	Modulus of elasticity. Poisson's ratio. Inelastic or creep behaviour. Tensile and shear strengths.
<i>Physical</i>	Size. Shape. Surface texture. Particle size distribution. Volumetric stability. Shrinkage and swelling. Thermal movement. Porosity. Specific gravity.
<i>Chemical</i>	Chemical composition.
<hr/>	
<b>PROPERTIES OF AGGREGATE-PASTE INTERFACE</b>	
Aggregate-paste bond strengths in tension and in shear.	
<i>Adhesive bond strengths</i>	Size, surface texture, and shape of aggregate.
<i>Cohesive bond strengths</i>	Chemical composition of paste and aggregate.
<hr/>	

Mechanical strength is commonly considered the most valuable property of concrete, since it usually gives an overall picture of the quality of concrete. The relation between the compressive strength and the gel-space ratio is shown in Fig. 10. The gel-space ratio is defined as the ratio of the volume of the hydrated cement paste to the sum of the volumes of the hydrated cement and of the capillary pores. It can be seen that strength is approximately proportional to the cube of the gel-space ratio, and the value of  $234 \text{ MN/m}^2$  represents the intrinsic strength of gel for the type of cement and specimen used. The relationship between the flexural and compressive strengths depends on the type of coarse aggregate (Fig. 11), since the properties of aggregates, especially its surface texture, affect the ultimate strength.

The cracking tendency depends not only on the potential contraction but also on the extensibility of concrete, its strength and its degree of restraint to the deformation that may lead to cracking. The schematic pattern [29] of crack development when stress is relieved by creep is shown in Fig. 12. Cracking can be avoided if the stress induced by shrinkage and reduced by creep, is at all times smaller than the tensile strength of the concrete. Fine cracks in fractured concrete, if allowed to close without tangential displacement, will heal completely under moist conditions (Fig. 13). This autogeneous healing [41] is probably due to the hydration of the hitherto unhydrated cement, and may also be aided by carbonation. Although full recovery can take place at different ages, it appears that the rate of healing decreases with increasing age of the material. Healing without a loss of strength has been observed at ages up to three years.

Typical values of permeability of concrete are given in Table 9.

TABLE 9 - TYPICAL VALUES OF PERMEABILITY OF CONCRETE [Ref. 11]

Cement content		Water-cement ratio	Permeability $10^{-12} \text{ m/s}$
$\text{kg/m}^3$	$\text{lb/yd}^3$		
156	263	0.69	8
151	254	0.74	24
138	235	0.75	35
223	376	0.46	28

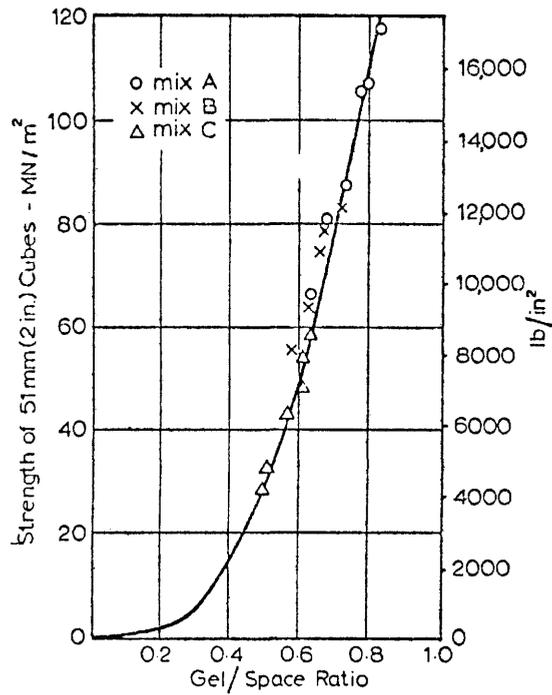


FIGURE 10 - RELATION BETWEEN THE COMPRESSIVE STRENGTH OF MORTAR AND GEL-SPACE RATIO [Ref. 30]

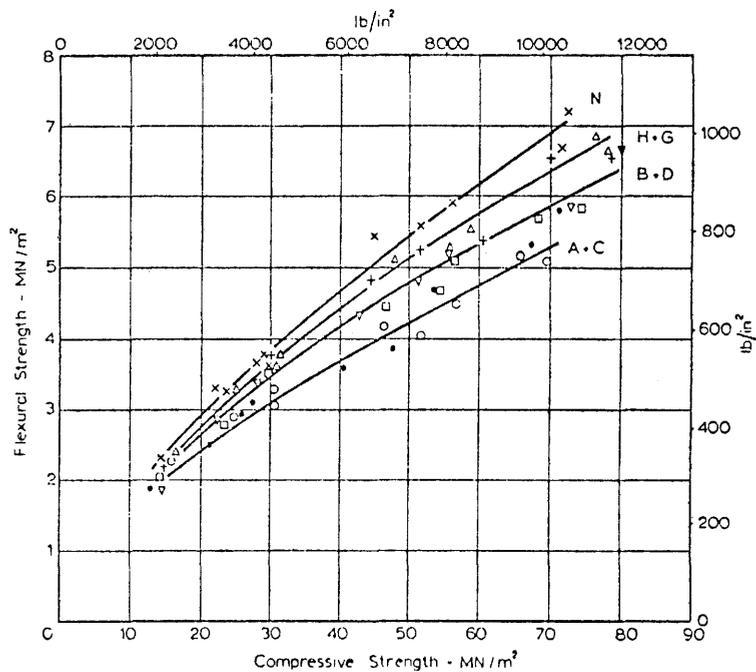


FIGURE 11 - RELATION BETWEEN FLEXURAL AND COMPRESSIVE STRENGTHS FOR CONCRETES MADE WITH DIFFERENT AGGREGATES [Ref. 29]

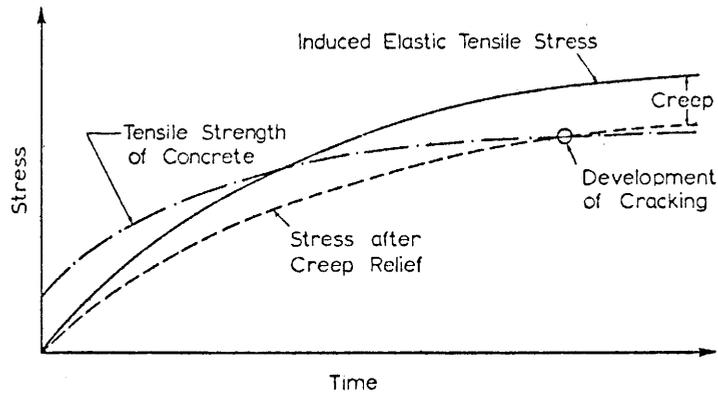


FIGURE 12 - SCHEMATIC PATTERN OF CRACK DEVELOPMENT WHEN TENSILE STRESS DUE TO RESTRAINED SHRINKAGE IS RELIEVED BY CREEP [Ref. 11]

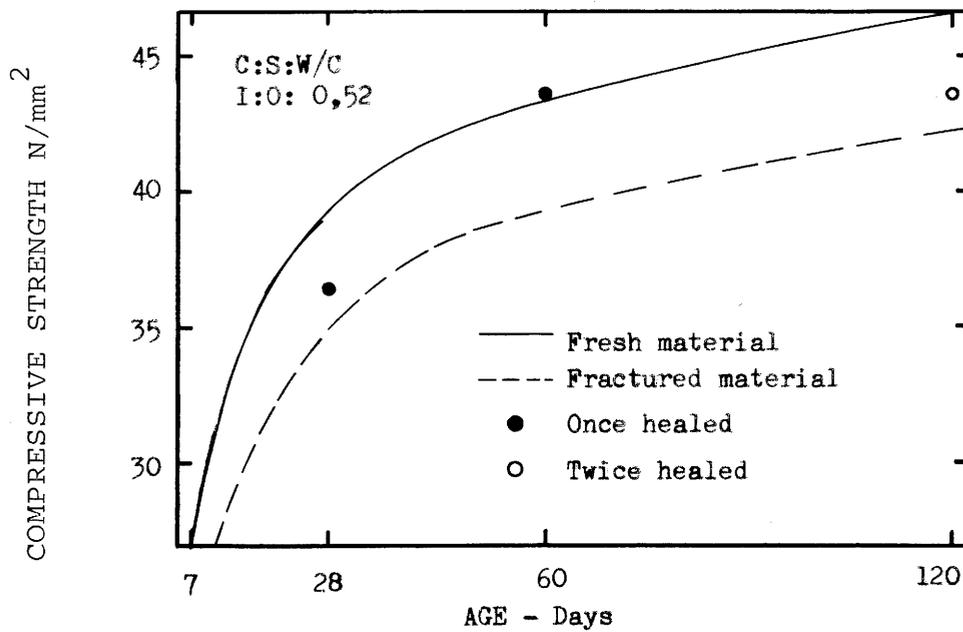


FIGURE 13 - STRENGTH-AGE RELATIONSHIPS FOR FRESH, FRACTURED, HEALED AND REHEALED MORTARS [Ref. 41]

Permeability of concrete is of interest in relation to water-tightness or liquid-retention, penetration of concrete by materials in solution, and also with reference to the problem of hydrostatic pressure in the interior of concrete structures. Since aggregate particles are enveloped by the cement paste in fully compacted concrete, it is the permeability of the paste that has the greatest effect on the permeability of the concrete. Concrete durability is the most important factor of the long time safety of concrete structures. Generally, concrete durability depends on a number of physical and mechanical properties of the material: porosity, permeability, absorptivity, capillarity, tensile strength and bond of the components.

### 3. STABILITY OF STRUCTURE

Under many conditions the deterioration of concrete structure is not due to any single cause, but arises from the combined action of a number of potentially destructive agents. The internal chemical reactions of concrete and the chemical resistance of concrete to external aggressive media will be described with a view to understanding long-term durability of concrete structure.

#### 3.1 ALKALI-AGGREGATE AND ALKALI-CARBONATE REACTION

Some deleterious chemical reactions [42,43,44] between the aggregate and the surrounding cement paste have been observed. The reaction starts with an attack on the siliceous minerals in the aggregate by the alkaline hydroxides derived from the alkalis ( $\text{Na}_2\text{O} + \text{K}_2\text{O}$ ) in the cement. The mechanism involves hydroxide ion attack on the susceptible aggregates, resulting in alkali-silicate reaction products that develop pressure, expand, and crack in cement paste.

The reactive aggregate materials occur in: opaline, chalcedonic cherts, siliceous limestones, rhyolites and rhyolitic tuffs, dacite and certain phyllites.

An expansive type of reaction in concrete [45] under moist conditions has been found to occur between alkalis from the cement and certain, uncommon, types of dolomitic limestones which from their physical properties appear to form satisfactory aggregates. This reaction is quite distinct from the alkali-siliceous aggregate reaction and the aggregates involved are limited to certain fine-grained, argillaceous, dolomitic limestones.

#### 3.2 CARBONATION OF CONCRETE

$\text{Ca}(\text{OH})_2$  in the concrete carbonates to  $\text{CaCO}_3$  by reaction with carbon dioxide in the presence of moisture and other unhydrated or hydrated compounds. Also hydrated silica, alumina, and ferric oxide can be produced as an ultimate product of total carbonation [46,47,48].

Such a complete decomposition of calcium compounds in hydrated cement is chemically possible even at the low pressure of  $\text{CO}_2$  in normal atmosphere, however carbonation penetrates beyond the exposed surface of concrete only extremely slowly by a diffusion process.

Carbonation is accompanied by an increase in the weight of the concrete and by shrinkage. Carbonation shrinkage (Fig. 14) is probably caused by the dissolving of crystals of  $\text{Ca}(\text{OH})_2$  while under a compressive stress which is imposed by the drying shrinkage and depositing of  $\text{CaCO}_3$  in spaces free from stress. The compressibility of the cement paste is thus temporarily increased. Carbonation of hydrates present in the gel does not contribute to shrinkage as the reaction does not involve solution and reprecipitation [49].

The depth of carbonation of fully compacted and normal cured concrete is largely determined by temperature and by the water-cement ratio in an almost linear relationship. Depth is also determined by the type of cement [50]: other things equal, carbonation penetrates deeper in concretes made with blast furnace slag cements and pozzolanic cements than in Portland cement concretes.

Carbonation of concrete results in increased strength and reduced permeability possibly because water released by carbonation aids the process of hydration and  $\text{CaCO}_3$  reduces the voids within the cement paste. The carbonation of dense concretes is not likely to proceed beyond a surface layer and the main body of the structural material remains unaffected.

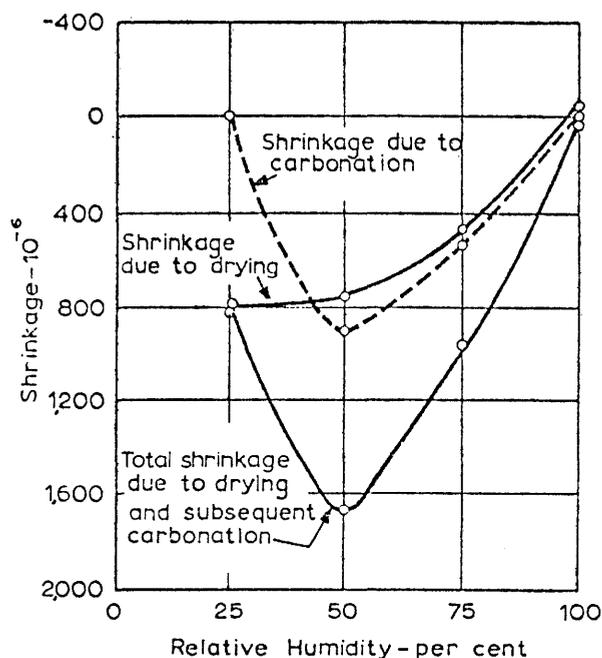


FIGURE 14 - CARBONATION SHRINKAGE AT DIFFERENT RELATIVE HUMIDITIES [Ref. 11]

### 3.3 CHEMICAL ATTACK BY AGGRESSIVE MEDIA IN GROUNDWATER

The possibility and the intensity of chemical attack depend on solubilities, concentrations and dissociation constants of aggressive media and on the same parameters corresponding to the reaction products under normal conditions. The effects of major cationic and anionic compounds found in groundwaters of potential repository sites in Switzerland mentioned in Chapter 4 on mechanisms of deterioration in the concrete structure will be examined in the following.

#### 3.3.1 SULPHATE ATTACK

Attack of concrete by the groundwater containing alkali, magnesium and calcium sulphates can take place where the sulphate reacts with  $\text{Ca}(\text{OH})_2$  and calcium aluminate hydrate. The mechanism of the alkali and/or magnesium sulphate attack on concrete seems to proceed through a front of

ettringite penetration which causes cracks. Afterwards gypsum and/or brucite crystallize in the cracks causing either further expansion or the filling of cracks and pores [51].

The expansion of concrete due to sulphate attack can be ascribed to (i) the formation of sulphotoaluminate, (ii) the formation of gypsum, (iii) the formation of brucite, (iv) the formation of hydrated silica and (v) other reactions catalysed by the sulphate ions. The products of the reactions, gypsum and calcium sulphotoaluminate have a considerably greater volume than the compounds they replace so that the reactions with the sulphates lead to expansion and bursting of the concrete [52].

The rate of sulphate attack increases with concentration of the solution, but beyond a concentration of about 0.5 percent of  $\text{MgSO}_4$  or 1 percent of  $\text{Na}_2\text{SO}_4$  the rate of increase in the intensity of the attack becomes smaller [29]. The effects of mixtures of sulphates ( $\text{N}\bar{\text{S}}$  to  $\text{M}\bar{\text{S}}$ ) are in some way 'sub-tractive' or conversely reduce the attack of each of the two salts acting alone.

It has been assumed that expansive monosulphate ( $\text{C}_3\text{A} \cdot \text{CaSO}_4 \cdot 11 \text{H}_2\text{O}$ ) is formed in cement paste by reaction of  $\text{C}_4\text{AH}_{13}$  with sufficiently concentrated  $\text{SO}_4^{2-}$  ions by an anionic exchange process [53]. Further increase of  $\text{SO}_4^{2-}$  ion concentration may transform monosulphate into secondary harmless ettringite by a through-solution process, its crystals precipitating in pores. If the CH concentration in the liquid phase is high, the lowered solubility of  $\text{C}_4\text{AH}_{13}$  hinders the accommodation of monosulphate in pores.

The vulnerability of concrete to sulphate attack can be reduced by the use of cement low in  $\text{C}_3\text{A}$ . Improved resistance to sulphate attack is also obtained by the addition of or even by partial replacement of the cement by pozzolanas, which remove free  $\text{Ca}(\text{OH})_2$  and render the alumina-bearing phases inactive.

### 3.3.2 REACTION OF CHLORIDE SOLUTIONS

Chloride ions present in groundwater can penetrate hardened concrete with either deleterious effects due to reaction with the calcium aluminates in the cement, or beneficial effects due to changes in the form of hydration of calcium silicates. The water-cement ratio is one of the most important factors which influences the  $\text{Cl}^-$  ion penetration to the concrete surface layer for short durations of contact with chlorides, whilst the type of cement has a major influence in deeper penetration for longer duration of contact [54].  $\text{Cl}^-$  ionic diffusion depends not only on the permeability and binding capacity of the  $\text{Cl}^-$  ions, but also on the ion-exchange capacity of the system, i.e. of the cement paste.

Monochloroaluminate, which is first formed and crystallized in chloride attack on concrete, due to the more rapid diffusion of  $\text{Cl}^-$  ions, is unstable in the presence of  $\text{SO}_4^{2-}$  ions, so that afterwards it is transformed into expansive ettringite [55]. Although the diffusion rate of  $\text{Cl}^-$  ions is 10 to 100 times faster than that of  $\text{SO}_4^{2-}$  ions, sulphate attack caused by  $\text{Na}_2\text{SO}_4$  solutions is much greater than chloride attack produced by  $\text{NaCl}$  solutions on cement, as calcium sulphoaluminate hydrate is less soluble than calcium chloroaluminate hydrate [56]. A large quantity of chlorides in the ocean environment inhibit the expansion of the concrete in the presence of sulphate solution, which is attributed to the greater solubility of gypsum and calcium sulphoaluminate in chloride solutions. Serious deteriorations occur only when the formed compounds containing chloride are highly expansive in nature.

### 3.3.3 ACTION OF CARBONIC WATER

The attack of carbonic water on hardened concrete depends partly on the content of bicarbonate and free carbon dioxide in water, and partly on the carbonation of the cement paste. For a constant content of bicarbonate in the water the lime-removing power increases with the content of free carbon dioxide. When the content of free carbon dioxide remains unchanged the dissolving power increases as the content of bicarbonates in the water falls.

If the solution is not saturated with calcium bicarbonate, excess  $\text{CO}_2$  may attack and dissolves calcium carbonate. However this attack [57] progresses only up to reach saturation in calcium bicarbonate, so that only a part of the 'excess'  $\text{CO}_2$  acts more or less depending on the lower or higher initial concentration of  $\text{Ca}(\text{HCO}_3)_2$ .

Excess  $\text{CO}_2$  of aggressive waters may attack  $\text{Ca}(\text{OH})_2$  from cements, but calcium carbonate formed precipitates in the pores of the cement paste. This is a way to compact concrete and consequently carbonation by carbonic waters may have a beneficial effect for concrete, provided that no leaching of calcium bicarbonate occurs and attack stops by a compaction effect near to the surface of the concrete [58].

Carbonation of a cement surface by exposure to air reduces the action of waters which have a high solvent power. The corrosion of concretes in media containing  $\text{SO}_4^{2-}$  is decreased by carbonation with  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  ions as a result of binding the  $\text{Ca}^{2+}$  in  $\text{CaCO}_3$  rather than  $\text{CaSO}_4$ . The relative low corrosion rate of concretes in groundwaters containing  $\text{SO}_4^{2-}$  in the Crimean peninsula [42] was attributed to the presence of  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  as a result of the contact of the groundwater with atmospheric  $\text{CO}_2$  and carbonate rocks. The presence of sodium bicarbonate was found somewhat to decrease attack by sulphate solutions suggesting that carbon dioxide content of seawater plays some part in decreasing its aggressive effect [59].

### 3.4 CORROSION OF REINFORCEMENT

If the concrete cover over the embedded steel is thick and dense, it can provide the steel with long-term protection against corrosion and will contribute to the production of good bond between the concrete and steel. The protecting effect of the concrete cover against corrosion is of a physical and chemical nature and its functions may be summarized as:

- to provide chemical protection by forming a thin protective passivating film of  $\gamma\text{-Fe}_2\text{O}_3$  on the steel surface

- to provide a physical barrier to the ingress of moisture, oxygen and carbon dioxide and to the conductivity of electrolytic currents
- to provide a physical and chemical barrier to the ingress of aggressive media.

Under certain circumstances, however, this protective barrier can be disrupted either by a lowering of pH of the water phase in concrete by carbonation or by a penetration of aggressive ions including chloride ions to the steel surface. While carbonation of concrete is normally not a problem, it is well established that even very small concentrations of chloride ions are able to destroy the passivating film. The presence of chloride ions raises the pH required to stabilize the passive film to a value which may exceed that of a saturated calcium hydroxide solution in hardened concrete; therefore the chloride ions may stimulate corrosion.

The corrosion of steel is an electrochemical process associated with the presence of anodic and cathodic areas arising from inhomogeneities in the surrounding liquid medium or even in the steel surface itself. The extent to which these reactions proceed depends upon the conductivity of the electrolyte and the difference in potential between relative areas of anodes and cathodes in the complicated system of galvanic cells developing along the steel [60,61, 62].

The strong anodic polarisation observed in chloride-free concrete does not occur when chloride is present and the corrosion is no longer controlled by anodic polarisation but depends on the velocity of the cathodic reaction which is governed by the availability of oxygen [63]. Once the passivating film is disrupted in high chloride environments such as ocean or certain underground environments, the electrical resistivity of the concrete and the availability of oxygen at the steel surface will be the main controlling factors to further steel corrosion [64,65]. For concrete structures in the oceans it appears that the rate of steel corrosion is primarily controlled by concentration polarization caused by diffusion of dissolved oxygen through the concrete cover.

In the continuously submerged zone of concrete in the oceans steel corrosion [66] is almost negligible due to slowness of transfer of dissolved oxygen through concrete which is completely wet. For a high quality concrete continuously exposed to seawater a protective coating will fairly soon form at the concrete surface due to an ion exchange taking place between the concrete and the seawater [67]. Such a coating may also successively reduce the diffusion of oxygen to a substantially lower level. The final results of the corrosion process is the formation of a thick rust layer which exerts sufficient tensile forces within the concrete to crack and cause spalling of the concrete cover.

4. POSSIBLE ENVIRONMENTAL CONDITIONS IN THE REPOSITORY SITE

The ability of a repository to provide long-term isolation of nuclear wastes depends on the effectiveness of one or more natural and engineered barriers. These barriers relate to the waste form and its container, structural concrete, the enclosing rock mass, and the length and character of the groundwater flow paths from the repository to the biosphere. Regarding possible hazards from volcanic activity, earthquakes and erosion, geologic and engineering knowledge seems ample to ensure that the probability of damage to a properly selected and well constructed repository is vanishingly small.

Geologic criteria for repository site selection were formulated by Brunton and McClain [68] for the Office of Waste Isolation (OWI) Program in 1977. Subsequently, draft revised criteria have been formulated by Battelle Memorial Institute Office of Nuclear Waste Isolation (ONWI) [69]. The criteria are arranged in three main categories: geological, engineering, and socio-economic, as given in Table 10, which includes the key subjects under each category. A number of factors in the evaluation process are considered for each of the criteria listed in the table.

TABLE 10 - SITE EVALUATION CRITERIA [Ref. 69]

Geological criteria	Engineering criteria	Socio-economic criteria
Geometry depth vertical extent lateral extent	Mechanical properties State of stress Seismicity Site development	Mineral resources Water resources Land resources
Stability uplift or subsidence faulting igneous activity		
Hydrology hydrological properties water content		
Geochemistry radiation reactivity		

#### 4.1 POTENTIAL REPOSITORY SITE

Geologic formations at mineable depths in the earth's crust are being viewed as possible media for disposal of nuclear waste, especially high-level nuclear waste. Table 11 shows the partition of research efforts between the various countries and geologic formations in the European Communities [70].

TABLE 11 - RESEARCH UNDERWAY ON WASTE DISPOSAL IN VARIOUS TYPES OF GEOLOGICAL FORMATIONS [Ref. 70]

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##### Clay Formations

- Belgium: Complete geological-geochemical-hydrological prospection of a site, shaft drilling and preparation of an underground cavern for in-situ testing, laboratory studies of mechanical-physical-chemical properties of clays and model studies of radionuclide diffusion.
- Italy: Geological prospection at Trisaia site, exploratory borehole drilling, in-situ tests of heat dissipation and laboratory studies.
- Denmark: Clay properties.

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##### Salt formations

- Federal Republic of Germany: In-situ testing (Asse mine), temperature distribution, convergence, stress analysis, brine migration, emplacement techniques for HLW canisters and material corrosion studies.
- Netherlands: Model studies, exploratory borehole drillings (planned) and risk assessment.

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##### Hard Rocks

- France: Geological prospection of three sites, modeling of radionuclide migration, artificial barriers and in-situ tests (hydrology and radionuclide transport).
- United Kingdom: Hydrology of fissured rocks, water composition and dating, repository-formation interaction modeling, in-situ tests of heat effects, corrosion tests and risk assessment.
-

It should be noted that, in general, the selection of a certain type of formation by a country does not reflect any commitment of the country for the final disposal solution for highly active solid radioactive wastes, but simply an optimized choice of its own resources, taking also into account the competences existing in the various national laboratories.

In the United States, bedded salt is considered the primary rock type for development of the first repository for commercially-derived, high-level radioactive waste [71]. The rock formations besides salt which currently seem favourable for waste disposal are granite, basalt, other crystalline rocks of igneous and/or metamorphic origin, tuff, clay and shale. A comparison of materials properties for two rock types as potential repository media is given in Table 12. Details of potential repository media are outlined in the following sections.

#### 4.1.1 BEDDED OR DOMED SALT

Salt has been for many years the rock most widely favoured for waste isolation because of its near-impermeability, its ease of mining, its high heat conductivity, and its ability to deform plastically so as to gradually fill cracks and other openings. The major uncertainty remains regarding the chemical stability of canisters and solid waste. In the presence of water that might collect in a salt repository. The danger here is not groundwater moving long distances through the salt, but water in tiny inclusions in the salt crystals and possible larger pockets that can be expected to move toward a source of heat, hence to collect around the canisters. The water would necessarily be a concentrated brine, probably of complex composition because of impurities in the salt; and at the high temperatures to be found near a canister would be highly corrosive. In this kind of environment the uncertainty regarding waste-groundwater is extreme, but uncertainty regarding flow of groundwater is less acute because of the impermeability of salt and its ability to heal fractures by plastic flow [72].

TABLE 12 - COMPARISON OF MATERIALS PROPERTIES DATA FOR TWO ROCK TYPES BEING STUDIED AS POTENTIAL REPOSITORY MEDIA [Ref 71]

Property	Granite	Argillite	Units
Bulk density	2.6	2.6	mg/m <sup>3</sup>
Porosity	0.5-2.0	9	vol %
Water content	0.8	3.5	wt %
Thermal conductivity	4	2.5	w/m K
Specific heat	1	1	kJ/kg K
Linear thermal expansion coefficient	7	12	$\times 10^{-6}/K$
Youngs modulus	70	7	
Poisson's ratio	0.25	0.35	---
Uniaxial compressive strength	200	40	MPa
Tensile strength	14	1.9	MPa

Note:

Materials data for basalt, granite and salt are from Agapito, Hardy and St. Laurent, 1977

Materials data for argillite are from Lappin and Cuderman, 1978

Water contents for granite and basalt are from Clark, 1966

Brines in the rock salt tend to be mobilized by thermal energy, either by fracture-decrepitation mechanisms, the migration of fluid inclusions or by dehydration of hydrous minerals. The presence of brines can be expected to increase the possibility of corrosion of canisters and leaching of waste, to weaken the rock strength, and to decrease sorptive properties of the host rock.

#### 4.1.2 GRANITE

Granite is commonly mentioned as an attractive alternative to rock salt for repository development because of its low permeability, its ability to maintain openings indefinitely, and its relative chemical inertness at the temperatures to be expected in a repository. The density of granite is about 2900 kg/m<sup>3</sup>, whilst a modulus of elasticity of granite is suggested as 32,000 megapascals for both horizontal and vertical directions. The compressive strength of the 'average' granite in the fairly sound conditions is about 125 megapascals and its tensile strength is about 17 megapascals on average. In general it appears that the higher the porosity, the lower will be the saturated strength, compared with the dry, or air-dry conditions.

Thermal analyses have shown that the temperature distributions outside the repository do not differ greatly even between such disparate rock types as salt and granite. Although the thermal conductivity of salt is approximately twice that of granite, the maximum temperature developed in granite could be lower than that in salt because the larger volumetric heat capacity in granite more than offsets its lower thermal conductivity.

The possibilities of granite have been explored more thoroughly in Sweden than elsewhere and the major uncertainty mentioned in Swedish reports concerns the unexpected large amounts of water that entered a cavity excavated in granite from cracks in the rock. Almost universally granite bodies are cut by fractures in many directions, some of them partly filled with crushed material and mineral crystals, but all of them permitting more movement of water than the solid rock between. The information on water composition from the STRIPA granite mine in Sweden shows that the groundwater at the deeper levels (330 m and below) had pH values rising

from 8.8 to 9.8, with increasing sodium, chloride, calcium and sulphate, and decreasing bicarbonate. These are attributed to 'rock-water interactions and the possible admixture of minor amounts of fossil seawater'. Groundwater movement is governed by the porosity and permeability of the rock mass through which the water moves and by the hydrologic boundary conditions controlling the flow. The Swedish work includes field experiments to measure the rate of water movement through fractured granite from one wall to another, and this kind of experiment seems the only reasonable way to learn how much groundwater flow to expect in a particular environment.

#### 4.1.3 BASALT

A third rock generally considered as a potential repository medium is basalt, which occurs in relatively thin flows, much fractured and separated by layers of rubble and sediment that are in part good aquifers for water movement. The main constituents from basalt repositories are aluminosilicate and ferromagnesium silicate minerals.

Exploration at the Hanford area in Washington [74] has shown that some flows at depth are thick enough to contain a repository and that many fractures are tightly filled with secondary minerals. Uncertainty regarding rates of water movement through fractured rock will be as serious at Hanford as in the Swedish granites, and possible waste-groundwater reactions may be more troublesome because more material would be dissolved from basalt than from granite by hot water in a repository.

#### 4.1.4 SHALE

The Eleana shale which underlies parts of the Nevada Test Site and the Conasauga shale which underlies part of the Oak Ridge Reservation are considered of interest [75]. Silica and alumina dominate the composition of shales as they also dominate the compositions of most igneous rocks.

The ratio of alumina to alkali in shales is usually greater than 1:1 whereas in igneous rocks it is close to 1:1. Alumina occurs in shales as clay minerals, alumino-rich and alkali-depleted, with some feldspar whereas in igneous rocks alumina occurs almost exclusively in feldspars. Alumino-silicate minerals act as scavengers for cesium and strontium which become immobilized as pollucite, powellite and feldspar [71]. Shale may act as chemical as well as physical barriers to the migration of radionuclides from the immediate vicinity of a waste canister.

#### 4.1.5 CLAY

A potential nuclear waste repository to be mined into the Boom clay formation underlying the nuclear plants of Mol has been proposed to study the safety probability in Belgium [76]. The clay formation of Boom belongs to the Repelian age of the Oligocene and is covered essentially by Miocene and pleistocene sands. In the Mol region, the clay of 109 m thickness is situated between 160 to 269 m below land surface.

The Centre d'Etude de l'Energie Nucléaire (CEN/SCK) at Mol has carried out first-phase studies on heat transfer, soil mechanics (feasibility of engineering the cavities), migration and sorption properties, corrosion problems, etc. and is constructing an experimental room at depth to carry out in-situ experiments, particularly heating experiments. A high resolution seismic reflection survey is presently being carried out to confirm the results of borehole investigations over the site area (i.e. absence of faulting and homogeneity of the Boom clay).

With regard to the excavation, CEN/SCK is concerned about the soft-supporting strength of clay and in general about the feasibility of constructing a cavity at great depth in clay. The repository is planned to be located at a depth of between 260 and 300 meters where the permeability is estimated at  $4 \times 10^{-5}$  centimeter per second. The overlying sands have a high glauconite content, giving them good sorption qualities.

The Trisaia Nuclear Research Center in Italy is investigating disposals in the marly clays of Plio-Pleistocene age. The permeability of this clay is on the order of  $10^{-8}$  centimeter per second and a heating experiment has confirmed that due to the poor thermal conductivity of the clay the waste would need to be stored above the ground for relatively long periods. Further studies are planned including the drilling of a deep borehole to obtain samples over the full depth of the clay formation.

#### 4.1.6 FRACTURED CRYSTALLINE AND ARGILLACEOUS ROCKS

Fractured crystalline and argillaceous rocks have been proposed as alternative host rocks for storage or disposal of high level radioactive waste. In a properly selected repository site the matrix porosity and permeability of these rocks should be such that no flow can occur through the rock blocks and hence the fracture system will provide the only pathway for radionuclides to migrate away from the repository. Based on the results of the borehole testing program at Stripa [77,78] the volumes of water moving through the fractured granite appears to be very small. The macro-permeability experiment in the Stripa mine in Sweden is part of the Swedish-American Cooperation Program on Radioactive Waste Storage in Mined Caverns in Crystalline Rock.

## 4.2 POSSIBLE GEOLOGIC CONDITIONS

A key consideration in the long-term safety disposal of nuclear wastes is their stability in the repository environment. From the standpoint of the waste isolation system the thermal period of a geologic repository is the most critical. The thermal period extends from the time of closure of the repository for several hundred years, during which the heat production of the high-level waste is dominated by decay of the fission products. It is during this period that the repository contents and surrounding areas are likely to be subjected to the greatest thermal, mechanical and chemical stress. Most physical and chemical changes within the waste form, structural concrete or host rock that would affect the security of isolation would be expected to proceed at the highest rate during this period.

A schematic diagram showing the influence of possible geologic conditions on the long-term stability of cements and concretes is illustrated in Fig. 16. The general environmental conditions that could exist for any waste emplaced in a geologic repository appear to be pressure and temperature in the near field and the far field, as well as the pressure of water in a reducing environment.

### 4.2.1 THERMAL AND PRESSURE ENVIRONMENT

Stresses in the host rock at the depth of burial will largely reflect the weight of the overburden, the tectonic history of the region, and rheologic properties of the rock. Fig. 16 shows the observed variation of vertical stress with depth based on the available data from strain-relief measurements [79]. The line corresponding to an average density of overburden of 2.7 g/cm is shown for comparison.

The horizontal stress will equal the vertical stress only if the rock is incapable of sustaining shear stress. The extent of deviation of the horizontal stresses from the vertical stress is limited only by the strength of the rock. For gravitational loading alone, the horizontal stresses [80] would be predicted to be much lower than the vertical, and would be expected to fall along the line at the left side of Fig. 17.

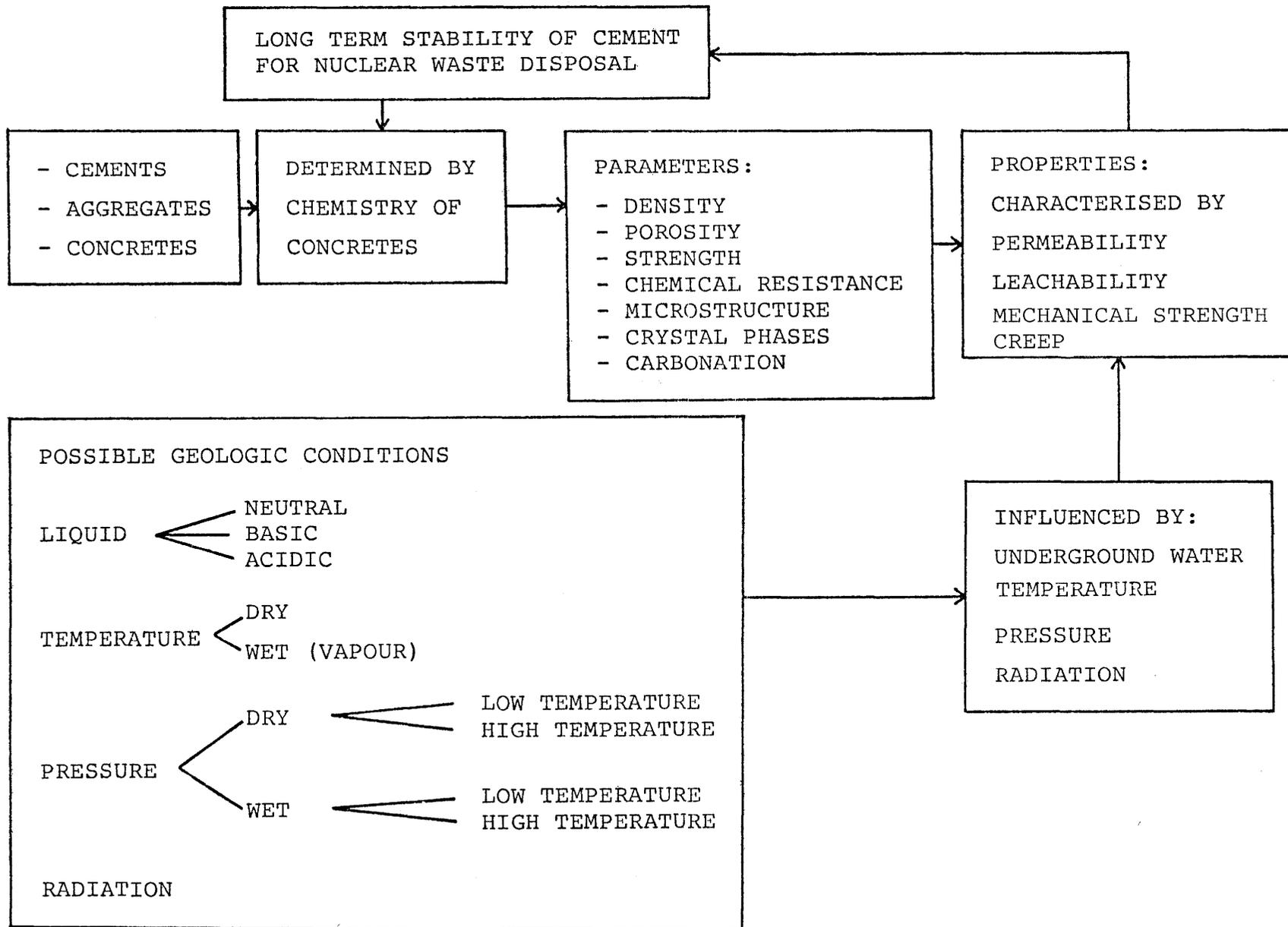


FIGURE 15 - SCHEMATIC DIAGRAM SHOWING THE INFLUENCE OF POSSIBLE GEOLOGIC CONDITIONS ON THE LONG-TERM STABILITY OF CEMENTS AND CONCRETES

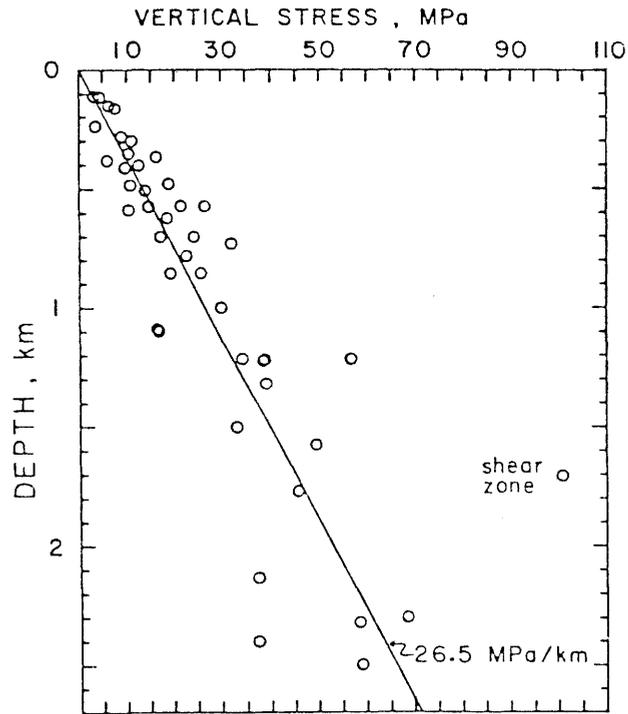


FIGURE 16 - VERTICAL COMPONENT OF STRESS FOR DEPTHS GREATER THAN 100 m [Ref. 79]

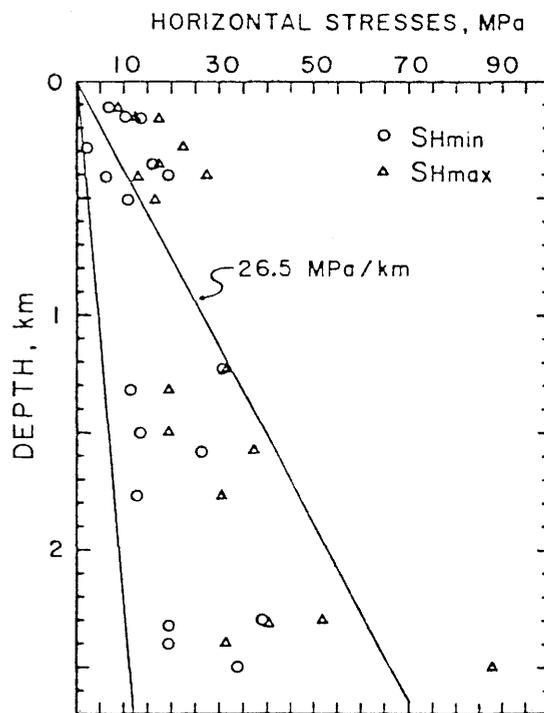


FIGURE 17 - HORIZONTAL STRESSES MEASURED IN SOUTHERN AFRICA [Ref. 80]

The values at depths below 500 m fall between that predicted and the overburden pressure; at more shallow depths the horizontal stresses exceed the vertical [81].

The temperature of the repository will most certainly be dictated by the thermal loading produced by the high-level waste emplaced in the repository. Individual areas might have higher or lower gradients than the normal geothermal gradient of 25°/km, depending upon the geologic characteristics and history of the region. The maximum temperature to be attained over tens of meters of rock host will probably be kept below 100°C by the choice of canister spacing or their thermal output. Temperatures around 100°C and pressures up to 30 MPa were suggested by NAGRA as an upper limit for the study of long-term stability of cement and concrete in a deep repository environment.

#### 4.2.2 GROUNDWATER IN DEEP CRYSTALLINE ROCKS

The most likely pathway by which radionuclides may reach the biosphere is by transport in moving groundwater [82,83,84]. A geologic medium would be chosen with low permeability so that any movement of groundwater would be slow, and a site would be selected to make the path that groundwater must travel to reach the biosphere very long. Walls of the repository can be treated, and openings into it can be sealed, to retard the entrance and escape of water.

As discussed in Chapter 3.3, the concrete used in the repository site can be attacked by chemical agents in groundwater. In Switzerland data on deep groundwaters are extremely scarce, and extensive programmes are being undertaken to improve this situation. Preliminary estimates may be obtained from analysis of some groundwaters in North Switzerland which appear to emerge from deep sources. For example, data on cations, anions, undissolved compounds, total dissolved compounds, dissolved gas, ion balance, physical and chemical parameters of groundwaters in Bürchau, Zurzach and Säckingen-Badquelle areas are given in Tables 13, 14, 15 and 16. It is likely that the groundwaters will be anoxic - i.e. the concrete will be in a reducing environment except for a brief period immediately after closure.

TABLE 13 - CATION ANALYSES OF GROUNDWATERS IN BÜRCHAU, ZURZACH AND SÄCKINGEN-BADQUELLE AREAS

Quelle Analyse	Bürchau	Z u r z a c h		Säckungen-Badquelle	
	Prof. Dr. R. Haas	Institut Fresenius 1966	Prof. Dr. O. Högl 1970/73	Dr. W. Käss 1971	Dr's. Bäurle u. Neusel 1955
<u>Kationen (mg/l)</u>					
NH <sub>4</sub> <sup>+</sup>	-	-	0.008	1.30	0
Li <sup>+</sup>	-	1.18	1.2	5.89	4.27
Na <sup>+</sup>	11.7	299.30	290.0	844.9	1016
K <sup>+</sup>	-	6.71	7.9	82.1	81.236
Rb <sup>+</sup>	-	0.06	-	0.026	-
Cs <sup>+</sup>	-	0.05	-	-	-
Ag <sup>+</sup>	-	0.0016	-	0.001	-
Be <sup>2+</sup>	-	0.001	-	0.06	-
Mg <sup>2+</sup>	3.7	0.71	1.4	9.6	9.048
Ca <sup>2+</sup>	12.6	16.20	15.2	96.0	110.71
Sr <sup>2+</sup>	-	0.60	0.6	3.42	-
Ba <sup>2+</sup>	-	-	-	9.3	-
Sn <sup>2+</sup>	-	-	-	0.014	-
Pb <sup>2+</sup>	-	-	0.011	0.04	-
Cu <sup>2+</sup>	-	0.0003	0.004	0.006	-
Zn <sup>2+</sup>	-	0.006	0.0085	0.035	-
Mn <sup>2+</sup>	-	0.08	< 0.01	0.03	0
Fe <sup>2+</sup>	-	0.11	0.054	0.14	0.2245
Co <sup>2+</sup>	-	-	-	0.014	-
Ni <sup>2+</sup>	-	0.0008	-	0.014	-
Al <sup>3+</sup>	-	-	< 0.01	0.71	-
Y <sup>3+</sup>	-	-	-	0.014	-
V <sup>3+</sup>	-	-	-	0.014	-
Cr <sup>3+</sup>	-	-	-	0.014	-
Mo <sup>3+</sup>	-	0.003	0.003	0.014	-
Bi <sup>3+</sup>	-	-	-	0.014	-
Zr <sup>4+</sup>	-	-	-	0.04	-
Ge <sup>4+</sup>	-	0.003	-	0.014	-
Total	28.0	325.0157	316.3885	1053.714	1221.4885

TABLE 14 - ANALYSES OF ANION, UNDISSOLVED COMPOUND, TOTAL DISSOLVED COMPOUND AND DISSOLVED GAS OF GROUNDWATERS IN BÜRCHAU, ZURZACH AND SÄCKINGEN-BADQUELLE AREAS

Quelle Analyse	Bürchau	Z u r z a c h		Säckingen-Badquelle	
	Prof. Dr. R. Haas	Institut Fresenius 1966	Prof. Dr. O. Högl 1970/73	Dr. W. Käss 1971	Drs. Bäurle u. Neusel 1955
<u>Anionen (mg/l)</u>					
F <sup>-</sup>	-	11.60	10.4	-	-
Cl <sup>-</sup>	4.5	134.60	133.0	1361.6	1563.7
Br <sup>-</sup>	-	0.70	0.62	3.77	-
J <sup>-</sup>	-	0.02	0.005	0.04	-
NO <sub>3</sub> <sup>-</sup>	-	0.41	0.26	-	-
HCO <sub>3</sub> <sup>-</sup>	67.1	265.40	259.0	292.8	407.6
SO <sub>4</sub> <sup>2-</sup>	12.3	263.30	255.0	99.9	113.49
HPO <sub>4</sub> <sup>2-</sup>	-	0.01	0.05	-	0.2438
HASO <sub>4</sub> <sup>2-</sup>	-	0.22	0.23	-	-
Total	83.9	676.26	658.565	1758.11	2085.0338
<u>Undissoziierte Bestandteile (mg/l)</u>					
H <sub>2</sub> SiO <sub>3</sub>	9.7	33.00	30.00	24.00	39.11
HBO <sub>2</sub>	-	0.80	1.7	2.73	-
H <sub>2</sub> TiO <sub>3</sub>	-	0.0008	-	-	-
Total	9.7	33.8008	31.70	26.73	39.11
<u>Total gelöste feste Bestandteile (mg/l)</u>					
Kations	28.0	325.0	316.4	1053.7	1221.5
Anions	83.9	676.3	658.6	1758.1	2085.0
Undissolved compounds	9.7	33.8	31.7	26.7	39.1
Total	121.6	1035.1	1006.7	2838.5	3345.6
<u>Gelöste Gase (mg/l)</u>					
CO <sub>2</sub>	-	-	< 5	-	54.41
O <sub>2</sub>	-	-	0.0	-	-
H <sub>2</sub> S	-	-	0.0	-	-

TABLE 15 - ION BALANCE OF GROUNDWATERS IN BÜRCHAU, ZURZACH AND SÄCKINGEN-BADQUELLE AREAS

Quelle Analyse	Bürchau	Z u r z a c h		Säckingen-Badquelle	
	Prof. Dr. R. Haas	Institut Fresenius 1966	Prof. Dr. O. Högl 1970/73	Dr. W. Käss 1971	Drs. Bäurle u. Neusel 1955
<u>Ionenbilanzen (mval/l)*</u>					
Kationen					
NH <sub>4</sub> <sup>+</sup>	-	-	0,00	0.07	0.00
Li <sup>+</sup>	-	0.17	0.17	0.85	0.62
Na <sup>+</sup>	0.51	13.02	12.61	36.75	44.19
K <sup>+</sup>	-	0.17	0.20	2.10	2.08
Be <sup>2+</sup>	-	0.00	-	0.01	-
Mg <sup>2+</sup>	0.30	0.06	0.12	0.79	0.74
Ca <sup>2+</sup>	0.63	0.81	0.76	4.79	5.52
Sr <sup>2+</sup>	-	0.01	0.01	0.08	-
Ba <sup>2+</sup>	-	-	-	0.14	-
Fe <sup>2+</sup>	-	0.00	0.00	0.01	0.01
Al <sup>3+</sup>	-	-	0.00	0.08	-
-----					
Total	1.44	14.24	13.87	45.67	53.16
-----					
Anionen					
F <sup>-</sup>	-	0.61	0.55	-	-
Cl <sup>-</sup>	0.13	3.80	3.75	38.41	44.11
Br <sup>-</sup>	-	0.01	0.01	0.05	-
HCO <sub>3</sub> <sup>-</sup>	1.10	4.35	4.24	4.80	6.68
SO <sub>4</sub> <sup>2-</sup>	0.26	5.48	5.31	2.08	2.36
-----					
Total	1.49	14.25	13.86	45.34	53.15

\* nur Ionen mit  $\geq 0.01$  mval/l bei mindestens einem Wasser

TABLE 16 - PHYSICAL AND CHEMICAL PARAMETERS OF GROUNDWATERS  
IN BÜRCHAU, ZURZACH AND SÄCKINGEN-BADQUELLE AREAS

Quelle Analyse	Bürchau	Z u r z a c h		Säckingen-Badquelle	
	Prof. Dr. R. Haas	Institut Fresenius 1966	Prof. Dr. O. Högl 1970/73	Dr. W. Käss 1971	Drs. Bäurle u. Neusel 1955
<u>Physikalische und Summen-Parameter</u>					
Temperatur (°C)	20.5	38.9	39.9	30.4	29.3
Dichte (20°)	-	-	1.00085	-	-
Spez. elektr. Leitfähigkeit µs/cm	-	-	1 260	-	-
pH	6.8	-	8.0	-	6.47
Radioaktivität					
nCi/l	5.3	-	1.4	-	-
Bq/l	196	-	51	-	-
Trocken- rückstand (mg/l)	-	-	840	-	-

5. THE INFLUENCE OF ENVIRONMENT ON CEMENT AND CONCRETE

Concrete durability is the most important factor of the long-term safety of concrete structure. It is essential that concrete should withstand the conditions for which it has been designed, without deterioration by the repository environment, over a long period of years.

5.1 AGING DUE TO THE ENVIRONMENTAL EFFECT

Structural components of the hydrate composite can be modified to take on a form of greater stability. Bond strength increases with the age of concrete; it seems that the ratio of bond strength to the strength of the paste increases with age [85]. With the progress of hydration the permeability decreases rapidly because the gross volume of gel is approximately 2.1 times the volume of the unhydrated cement, so that the gel gradually fills some of the original water-filled space.

The relative humidity of the medium surrounding the concrete [29] affects the magnitude of shrinkage, as shown in Fig. 18.

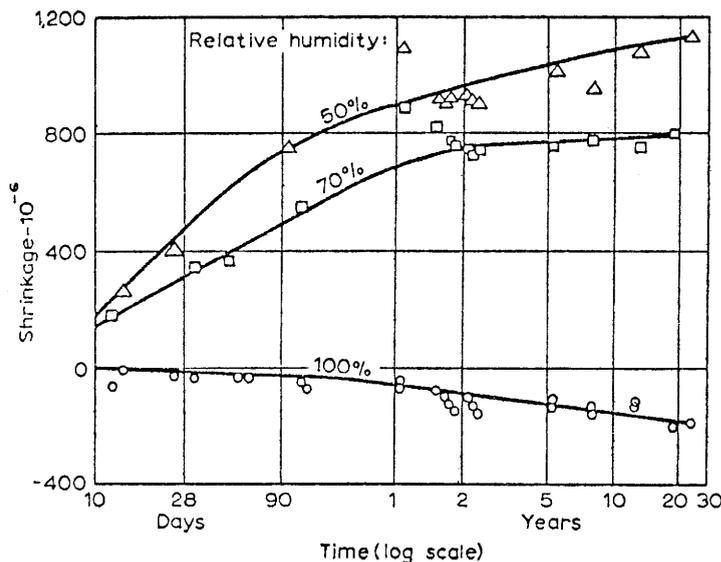


FIGURE 18 - RELATION BETWEEN SHRINKAGE AND TIME FOR CONCRETES STORED AT DIFFERENT RELATIVE HUMIDITIES [Ref. 29]

The same figure illustrates also the greater absolute magnitude of shrinkage compared with swelling in water: swelling is about six times smaller than shrinkage in air of relative humidity of 70 percent or eight times smaller than shrinkage in air at 50 percent. The expansion coefficient decreases with age due to a reduction in the potential swelling pressure owing to an increase in the amount of crystalline material in the hardened paste.

The age at which the load is applied greatly affects the magnitude of creep. This influence of age probably comes from the strength increase of concrete with age. Creep is higher the lower the relative humidity, which is illustrated in Figs. 19 and 20 for specimens cured at a relative humidity of 100 percent and then loaded and exposed to different humidities. The influence of relative humidity is much smaller or absent, in the case of specimens which have reached hygral equilibrium with the surrounding medium prior to the application of the load. Creep continues for a very long time, the longest determination to date indicating that a small increase in creep takes place after as long as 30 years. The rate of creep decreases, however, at a continuous rate, and it is generally assumed that creep approaches a limiting value after an infinite time under load.

Relationship between age and carbonation (neutralization) depth [86] shows that concrete based on ordinary Portland cement has a very small penetration depth during the period of 20 years.

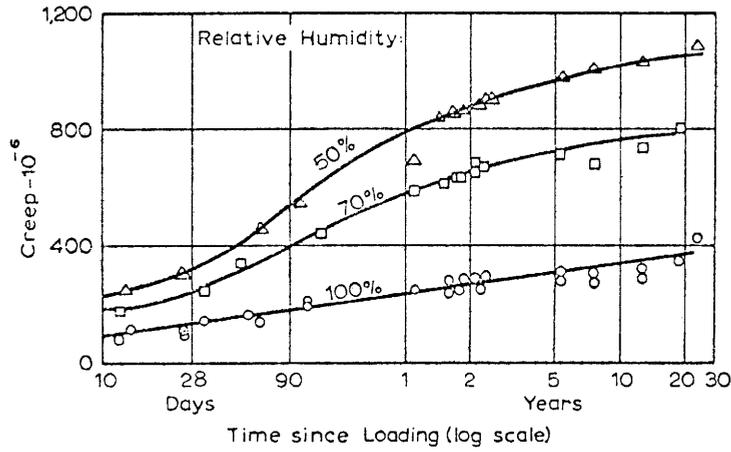


FIGURE 19 - CREEP OF CONCRETE CURED IN FOG FOR 28 DAYS, THEN LOADED AND STORED AT DIFFERENT RELATIVE HUMIDITIES [Ref. 11]

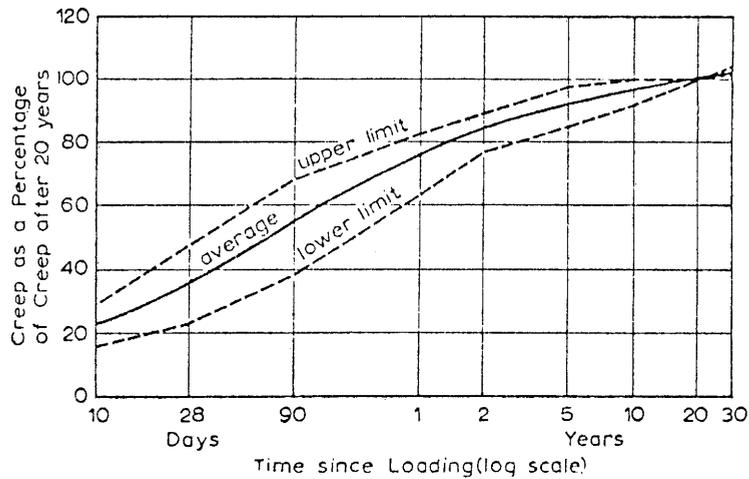


FIGURE 20 - RANGE OF CREEP-TIME CURVES FOR DIFFERENT CONCRETES STORED AT VARIOUS RELATIVE HUMIDITIES [Ref. 11]

## 5.2 THE EFFECT OF ELEVATED TEMPERATURE AND PRESSURE

### 5.2.1 PHASES FORMED IN THE CONCRETE

The hydration products of Portland cement,  $C_3S$  or  $\beta-C_2S$  in pastes at temperatures up to or somewhat around  $100^\circ\text{C}$  do not differ essentially from those formed at ordinary temperatures (described in Sections 2.1.1 and 2.1.2), though there are differences in morphology and microstructure.

Formation of C-S-H and tobermorite from mixtures of cement or  $\beta-C_2S$  with quartz has been studied with reference to geothermal and other borehole application [87-91]. Reaction passes through successive formation of various types of C-S-H to tobermorite, and high strengths have been obtained both with C-S-H (I) and with tobermorite as the binder. Chiocchio et al. [92] autoclaved  $\beta-C_2S$  with small amounts of  $C_3A$  and  $C_3F$ , and showed that some Al and Fe can enter the  $\alpha-C_2SH$  structure and that this generated resistance to sulphate attack.

### 5.2.2 PHYSICAL AND MECHANICAL STABILITY

High temperature produces a hydrated cement paste of low specific surface, about  $7000 \text{ m}^2/\text{kg}$ , indicating that the products of hydration are coarse and largely microcrystalline. High pressure steam-cured concrete [93] has a considerably reduced shrinkage, about 1/6 to 1/3 of that of concrete cured at normal temperatures (Fig. 21).

For mass-cured concrete there is no difference in modulus of elasticity in the temperature range 21 to  $96^\circ\text{C}$ . When water can be expelled from concrete, there is a progressive decrease in the modulus of elasticity, between about 50 and  $140^\circ\text{C}$ , as is illustrated in Fig. 22, which presents results from several sources [94,95] but all showing the same trend.

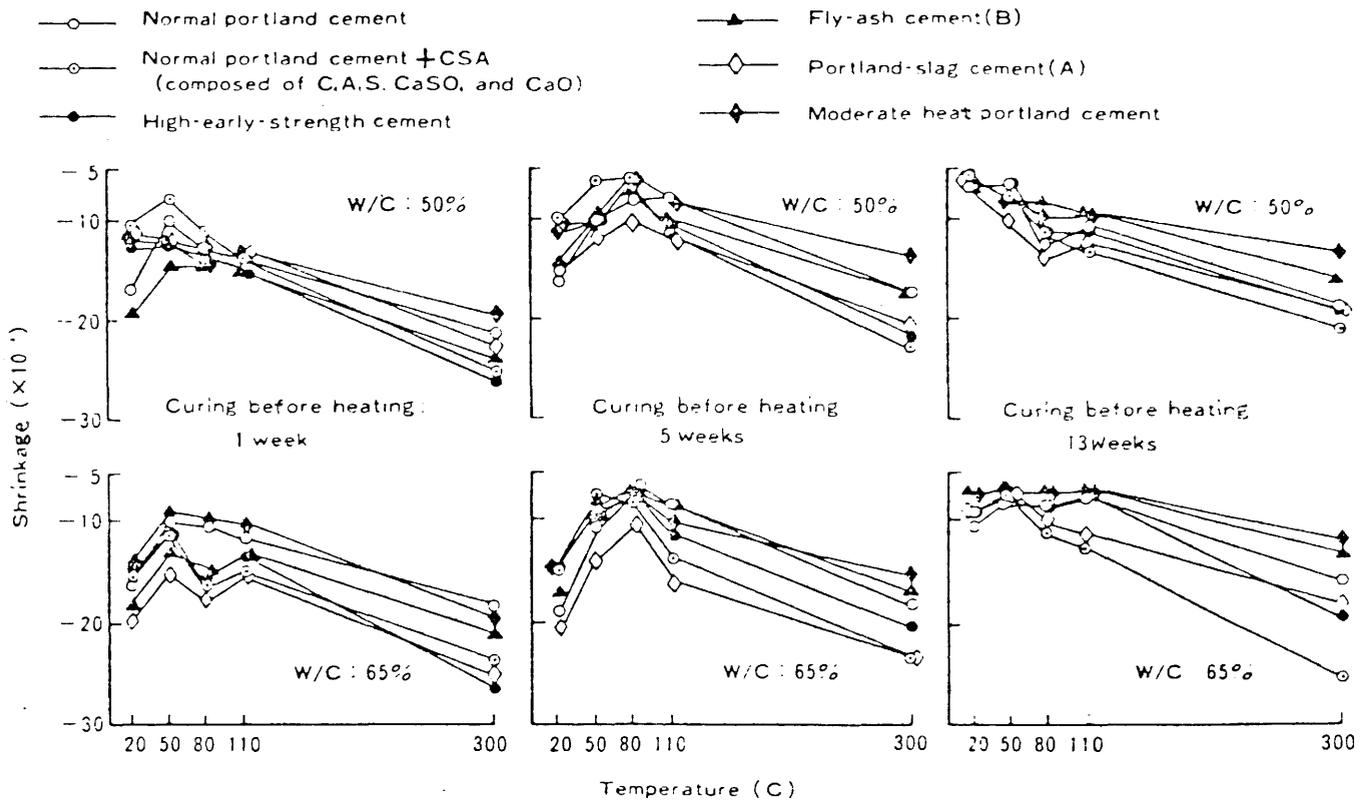


FIGURE 21 - RELATION BETWEEN SHRINKAGE AND TEMPERATURE [Ref. 93]

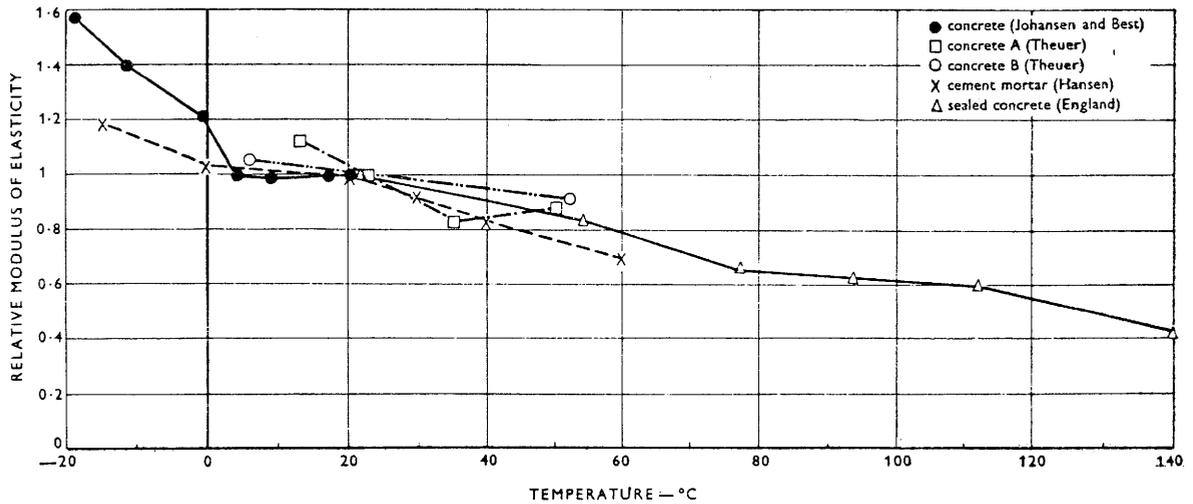


FIGURE 22 - EFFECT OF TEMPERATURE ON MODULUS OF ELASTICITY

Compressive strength and bond strength of concrete [96] after heating to high temperature are given in Figs. 23 and 24, which show a very little decrease in strength properties around 100°C. With high temperature and pressure 28-day strength on normal curing can be reached in about 24 hours. At the age of one year the strength of normally cured concrete is approximately the same as that of high-pressure steam-cured concrete of similar mix proportions.

The rate of creep [97] increases with temperature (Fig. 25). This behaviour is believed to be due to desorption of water from the surface of the gel so that gradually the gel itself becomes the sole phase subject to molecular diffusion and shear flow; consequently the rate of creep decreases.

### 5.2.3 CHEMICAL STABILITY

High pressure and temperature curing improves the resistance of concrete to sulphate attack [98]. This is due to several reasons, the main one being the formation of aluminates more stable in the presence of sulphates than those formed at lower temperatures. Further improvement in sulphate resistance is due to impermeability of the high pressure- and temperature-cured concrete and also to the existence of hydrates in a well-crystallised form.

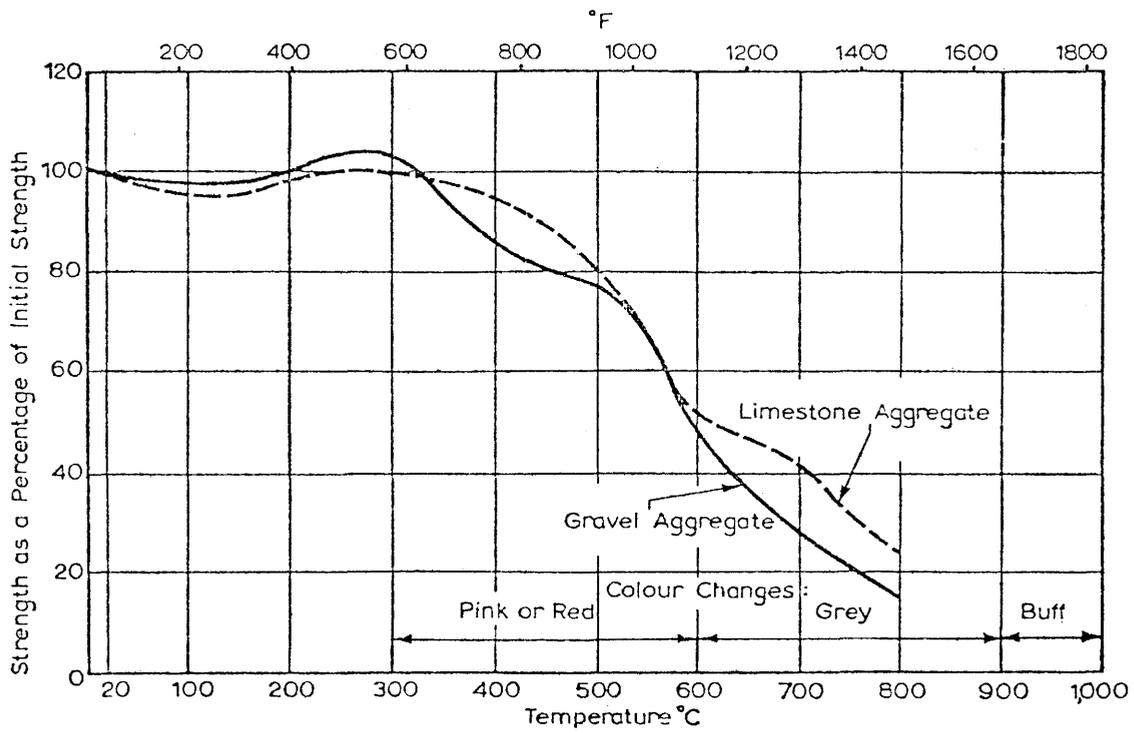


FIGURE 23 - COMPRESSIVE STRENGTH OF CONCRETE AFTER HEATING TO HIGH TEMPERATURES [Ref. 95]

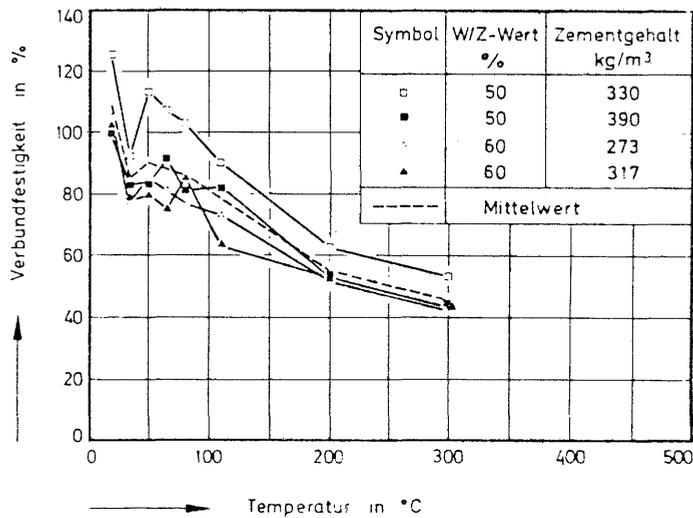


FIGURE 24 - BOND STRENGTH OF HEATED CONCRETE SPECIMENS [Ref. 96]

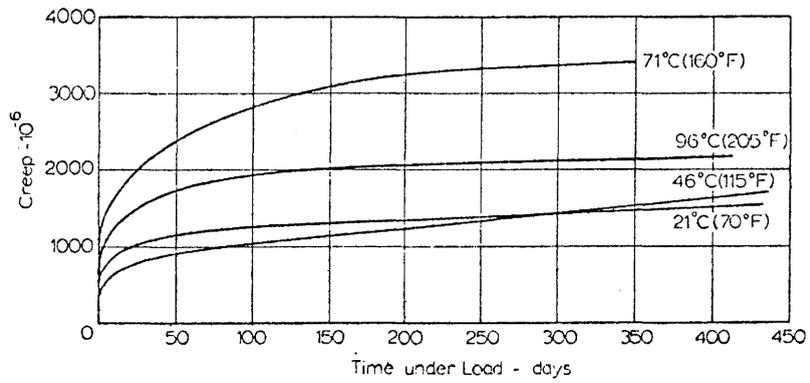


FIGURE 25 - RELATION BETWEEN CREEP AND TIME UNDER LOAD FOR CONCRETES STORED AT DIFFERENT TEMPERATURES [Ref. 97]

### 5.3 CHEMICAL AND PHYSICAL PROPERTIES OF THE INTERFACIAL REGIONS FORMED BETWEEN CONCRETE AND WALL ROCK

The effect of elevated pressures leads to an increase of the contact between concrete and rock surface and, when combined with elevated temperature, to an increase of the hydration rate.

Fig. 26 is a schematic diagram of the characteristic two-layer zone developed in the interfacial region between a non-reactive rock wall and Portland cement paste. The interfacial morphology [99] is characterized by a thin film of C-H(C-S-H) from which C-S-H particles appear to be growing. In addition to C-S-H particles, layer crystals of  $\text{Ca}(\text{OH})_2$  appear to attach the interfacial region to the bulk paste and thereby the rock to the bulk paste.

In order to determine the extent of chemical reaction as a function of curing temperature, pressure and time compositional scans by an electron microprobe were made on samples cured at 250°C and 51.7 MPa (Fig. 27). Chemical analyses [100] across the quartzite/cement contact (Fig. 27a) indicated a relatively sharp decrease in silicon over a distance of 50  $\mu\text{m}$  into the cement, and a sharp decrease in calcium over about the same range into the rock. Fig. 27b shows cross sections of the quartzite/cement contact zone for a sample cured three days. Minimum reaction was apparent under these conditions between the cement and the rocks. Surface roughness of the rock resulted in no major effect upon the basic structure of the interface [101].

Shear strength measurements [100] resulting in bond failure between Class J cement and Tuscarora quartzite appear to be more temperature dependent relative to those for Valentine limestone samples during the first seven days of curing. Hydrothermal curing for up to 21 days resulted in an increased degree of hydration of the cement paste. Samples cured at both 200°C and 250°C, 51.7 MPa resulted in similar bond strength measurement of  $7.8 \pm 1$  MPa after 21 days.

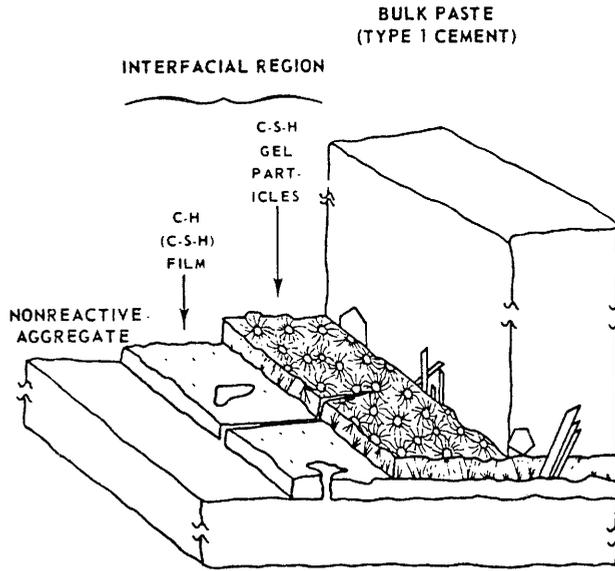


FIGURE 26 - SCHEMATIC DIAGRAM OF THE INTERFACIAL REGION FORMED BETWEEN A NON-REACTIVE SILICA SUBSTRATE AND TYPE 1 CEMENT PASTE [Ref. 99]

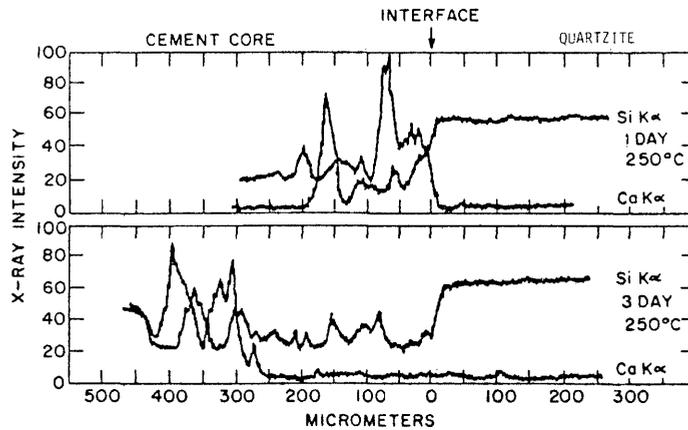


FIGURE 27 - ELECTRON MICROPROBE CROSS SECTIONS OF API CLASS J CEMENT/TUSCARORA QUARTZITE CONTACT OF SAMPLES CURED 1 AND 3 DAYS, (a) AND (b) RESPECTIVELY [Ref. 100]

#### 5.4 THE INFLUENCE OF GROUNDWATER ON STABILITY OF CONCRETE

The major aggressive chemical ions from the chemistry of groundwater described in section 4.2.2 appear to be  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$ . Chemical attack and deterioration mechanism by major compounds have already been mentioned in section 3.3.

The resistance of concrete to groundwater corrosion is very difficult to evaluate, owing to the complex nature of the corrosion phenomena involved. The formation of calcium sulphoaluminate in concrete is governed by the concentrations of sulphate and chloride in groundwater, and also by the mineral composition of Portland cement. In concretes made with Portland cement containing little  $\text{C}_3\text{A}$ , sulphoaluminate corrosion may be prevented completely by the chlorides. The role of gypsum corrosion is secondary here, because the solubility of gypsum is so high in the presence of  $\text{NaCl}$  that the crystallization of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  is no longer likely. This is why dense Portland cement concretes exposed to the groundwater deteriorate very slowly or not at all.

Magnesium corrosion is of minor importance, since the amount of magnesium is small enough to be precipitated in the form of  $\text{Mg}(\text{OH})_2$ . The high chloride content of groundwater may to some extent inhibit the expansion caused by sulphate attack, as discussed in Section 3.3. The influence of hydrocarbonates is definitely stronger. In sulphate solutions containing hydrocarbonates, the harmful trisulphate (ettringite) which is produced will form at a much slower rate than in solutions containing no carbonate. It is assumed that the hydrocarbonate combines with  $\text{Ca}(\text{OH})_2$  to form calcite which, precipitating on the surface, seals the pores of concrete. The formation of calcite is promoted by the presence of hydrocarbonate ions which in turn tends to curb sulphate attack. The resistance of concrete to groundwater corrosion thus depends essentially on the possibility of calcium sulphoaluminate formation. In this respect, the permeability and compactness of concrete play an important role.

If water flow or seepage rate is less than  $V = 0.1$  m/day the dissolved salts will tend to combine with the components of the hardened cement paste [60,102].

The pores of surface layer of concrete are sealed to a certain extent by the gypsum, calcite or  $Mg(OH)_2$  precipitated in them. As a result a natural protective layer is developed on and near the concrete surface. Carbonation of the surface is an essentially similar process. This natural protection will, however, exist only as long as the groundwater remains stagnant or the water flow is very low. It will be seen from the above considerations that in repository sites where seepage is slowed down or practically stopped by low permeability, concrete corrosion may be very slight, although no linear relationship could be established between seepage rate and the rate of corrosion.

The rates of chemical reactions increase rapidly with increasing temperature, and so does the detrimental chemical effect of aggressive water [42]. The degree of aggressivity of the chemical attack at elevated temperature and pressure is unknown.

The above discussion illustrates that the corrosion of concrete by groundwater is complex and not fully understood, but it can in general be stated that the resistance of concretes to corrosion increases with age.

## 5.5 RADIATION DUE TO THE RADWASTE

Concrete is widely and successfully used in radiation shielding for nuclear reactors. High density and the water naturally contained in concrete are the basic characteristics which make it an ideal construction material for blocking the most penetrating radiation, the gamma rays and fast neutrons, as well as alpha and beta particles and protons.

Concretes made with different types of cement and different types of aggregate show different radiation resistance. It can be stated with some certainty that the radiation resistance of concrete is mainly controlled by the radiation resistance of the aggregates.

An evaluation of the existing literature [103] on the effect of nuclear radiation on the mechanical properties of concrete indicates that neutron radiation with a flux of up to  $1 \times 10^{19}$  n/cm<sup>2</sup> and  $\gamma$ -radiation with a dose of up to  $2 \times 10^9$  rd does not cause deterioration of the mechanical properties of concrete. Fig. 28 shows the influence of neutron radiation on compressive strength of concrete samples.

The risk for destruction of concrete structure due to radiation from radwastes is extremely small [104]. Concrete lends itself well to the mechanical and structural requirements of nuclear applications without loss of strength and durability due to radiation.

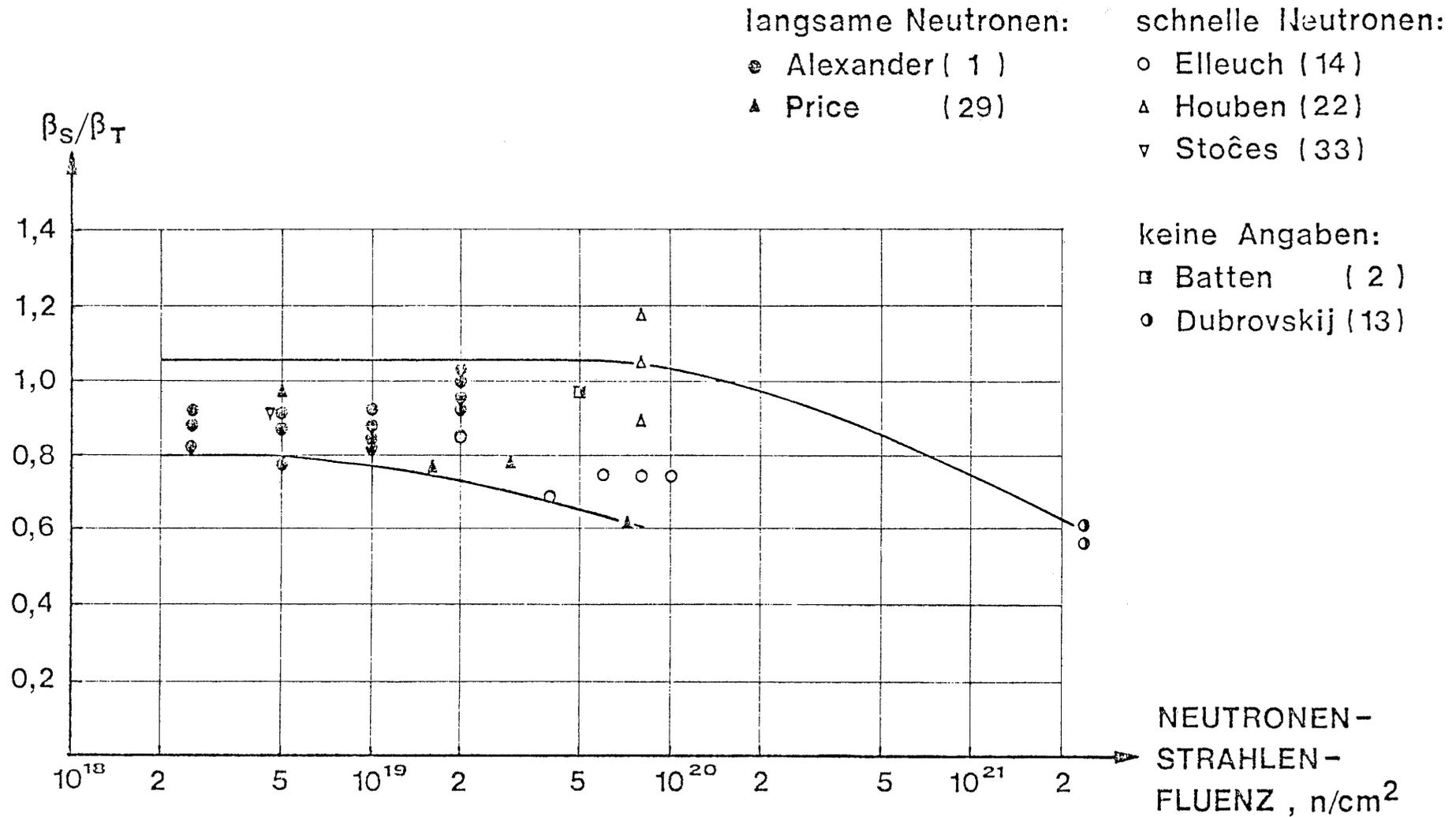


FIGURE 28 - INFLUENCE OF NEUTRON RADIATION ON COMPRESSIVE STRENGTH OF CONCRETE SAMPLES  
 ( $\beta_S$  is the compressive strength of radiated specimens, whilst  $\beta_T$  is that of control samples)

## 5.6 FIFTY YEARS PROPERTIES OF CONCRETE

The effect of age on the compressive strength of concrete [105-109] are compared in Figs. 29-30. Compressive strength of concrete stored outdoors generally increased with the age up to 50 years. The curves in Figs. 29 and 30 show that after about 6 months concrete stored outside has a higher strength than the comparable concrete stored indoors.

With full allowance for differences in water-cement ratios it is quite apparent that the strength increase gradually even after 50 years. All the concretes and mortars, which included a variety of cements, aggregates and mix proportions, showed remarkably good weathering qualities during the 50 year exposure period.

The durability of reinforced concrete construction [109,110] based on samples cut out from a 40 year old bridge has been evaluated. Penetration depth of chloride in concrete and the effect of chloride concentration on the durability of concrete structure are shown in Figs. 31 and 32 respectively. In Figure 32 the expected dependence of age and structures vs chloride content is illustrated along with appropriate practical data from bridges. Dams and piers and sewers being used in various countries [11,29,60], and concrete wharves in Norwegian harbours [66] are still in good condition after 50 years.

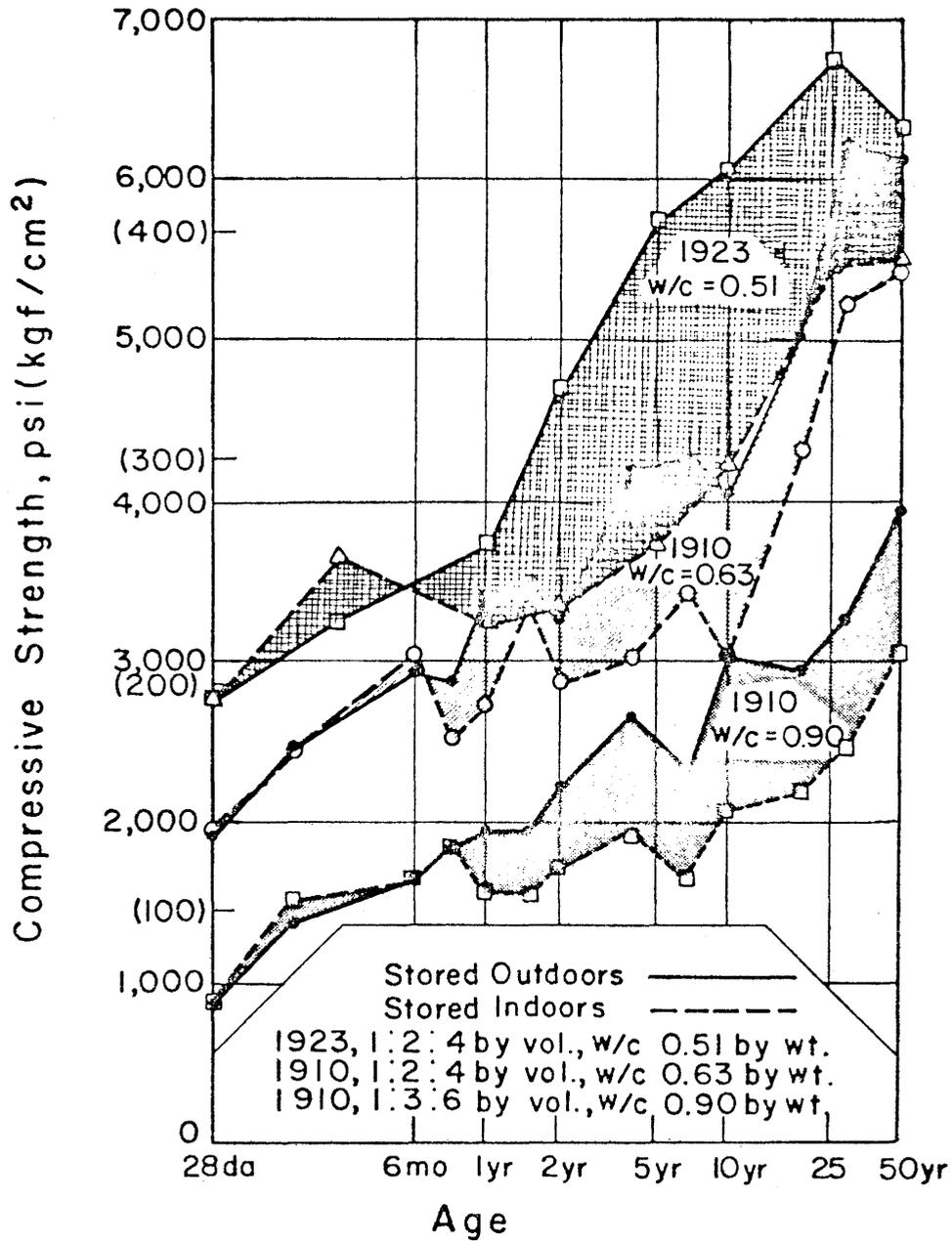


FIGURE 29 - COMPRESSION STRENGTH-AGE RELATIONS FOR SERIES A AND B CONCRETE STORED INDOORS AND OUTDOORS [Ref. 105]

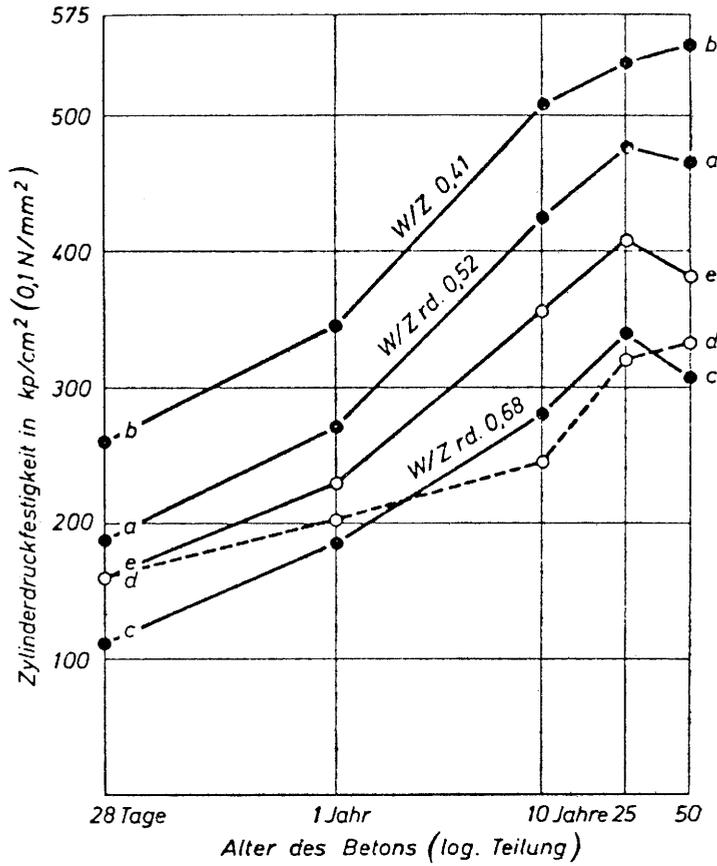


FIGURE 30 - COMPRESSIVE STRENGTH OF CONCRETE STORED OUTDOORS AND INDOORS VERSUS AGE UP TO 50 YEARS [Ref. 107]

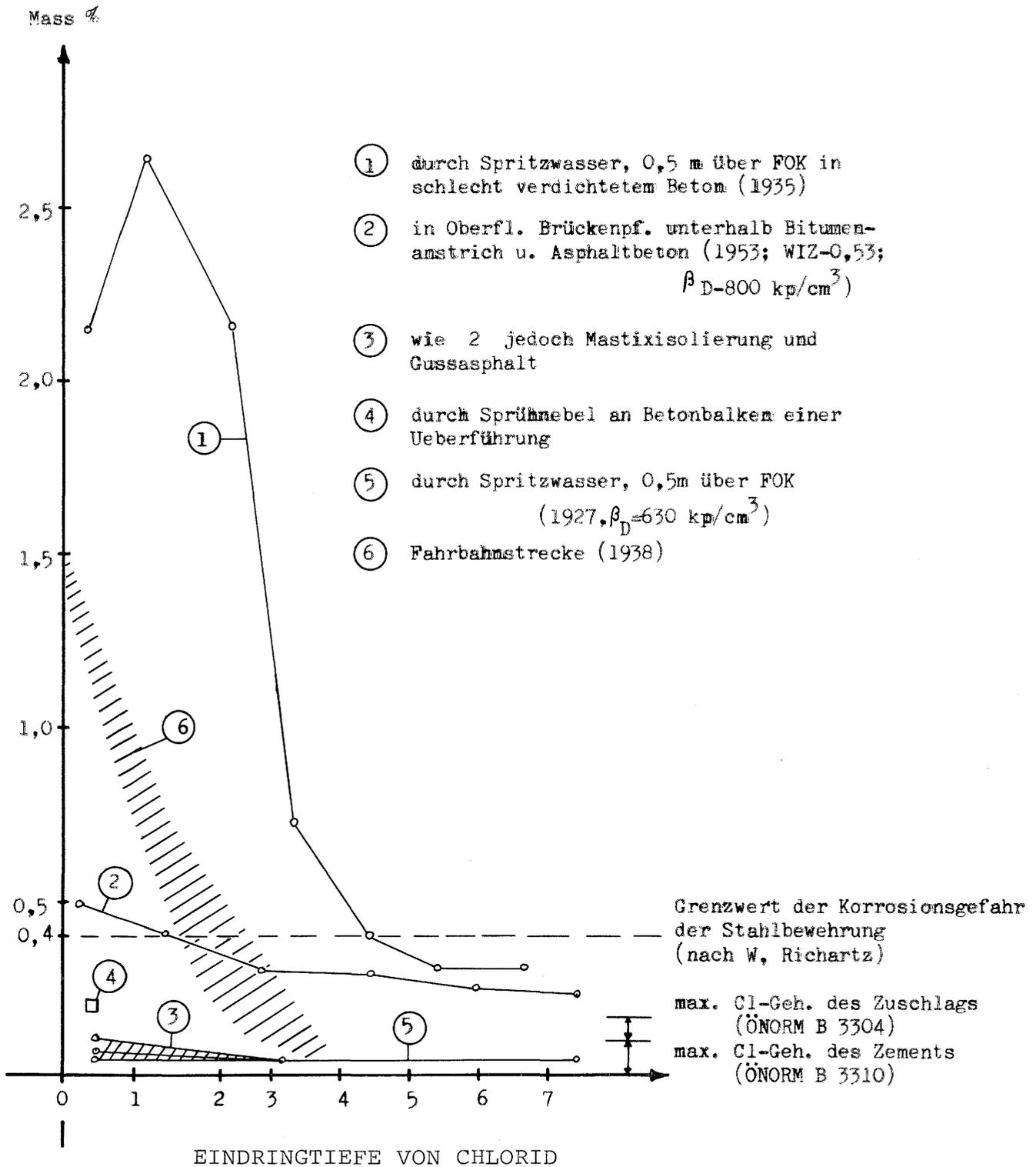
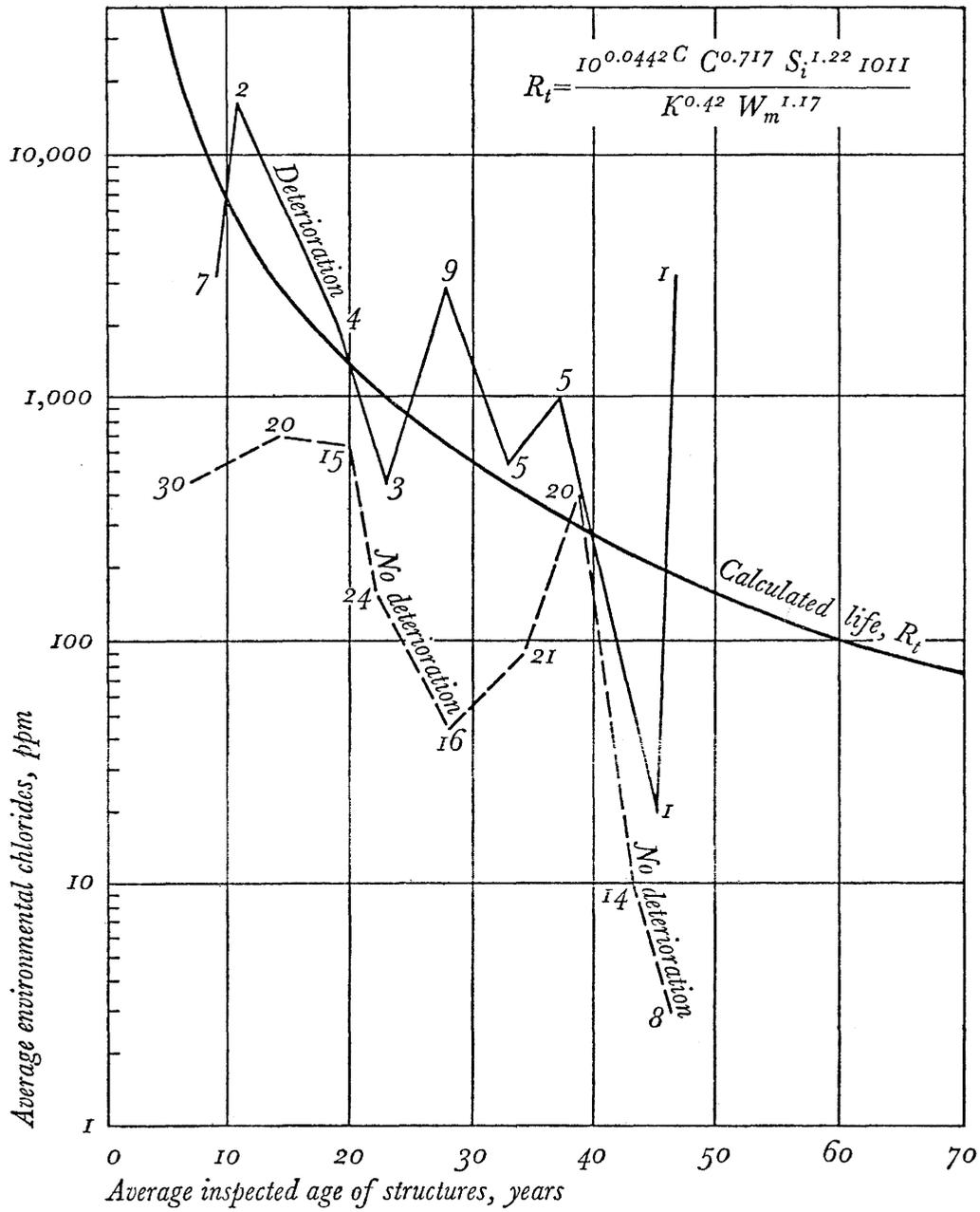


FIGURE 31 - PENETRATION DEPTH OF CHLORIDE IN CONCRETE [Ref. 109]  
(data from bridges and road ways)



Number indicates number of bridges inspected.  $C=6$ .  $S_i=2$ .  $W_m=22$ .

$R_t$  = Years to repair due to corrosion of reinforcing steel

$C$  = Sacks of cement per cubic yard

$K$  = Ppm chlorides

$S_i$  = Depth of concrete cover over reinforcing steel, inches

$W_m$  = Mixing water by per cent of concrete volume includes that contained by aggregate

FIGURE 32 - AVERAGE INSPECTED AGE OF STRUCTURES VERSUS ENVIRONMENTAL CHLORIDE CONCENTRATION [Ref. 110]

## 5.7 ANCIENT CONSTRUCTION

### 5.7.1 DURABILITY OF ANTIQUE CONSTRUCTION

Recently it was found that 7600 years ago about 60 tonnes of concrete was used for constructing floor of wooden houses at Lepenski Vir in Yugoslavia [111].

Cyclopean masonry of Greece was erected with the aid of some plastic material and there is evidence that the ancient Egyptians mixed gypsum with sand to make masonry mortars [112]. Lime was used at a very early period by the Greeks, and earlier still in Crete [113]. The early builders on the northern shores of the Mediterranean developed the skills of lime-burning. Such pure lime mortars and concretes harden slowly and often incompletely by reaction with the carbon dioxide of the air. A process employed on the Malabar Coast in India included mixing molasses with lime concrete in order to increase the hardness [114].

Hydraulic lime were produced by Greeks and Romans [115] by adding to the lime putty fine volcanic ash or crushed volcanic minerals. Both natural and artificial pozzolanas are composed chiefly of silica with some alumina in forms which on mixing with water will react readily with calcium hydroxide from the lime to give hydrated calcium silicates and aluminates.

The most famous of Roman buildings, erected in concrete in 27 BC, is the Pantheon, the 6 m thick walls of which are of tuff and pozzolana concrete thinly faced with brick, whilst the dome, 43.4 m in span, is cast solid in concrete containing pumice and pozzolana. Roman monuments [116] such as the bridges of Fabricius, Aemilius, Elius and Milvius, the arches of Claudius and Trajan at Ostia and Nero at Antium, together with many maritime works built in the time of the Roman Emperors (some of which, such as those erected by Trajan at Ancona and Civitavecchia, are in use today) all stand as a tribute to the permanence and durability of lime-pozzolana mortars shown during the period of 2000 years.

### 5.7.2 PROPERTIES OF ROMAN CONCRETE

Roman cement is made from lime marls containing considerable quantities of clay minerals; it is burnt at temperatures below the sintering point. The composition of a typical Roman cement [60] is as follows: CaO 45-54%, SiO<sub>2</sub> 22-35%, Al<sub>2</sub>O<sub>3</sub> + Fe<sub>2</sub>O<sub>3</sub> 10-16%, MgO 1-5%. The temperature, at which Roman cement is burnt, hardly exceeds 1100°C. Owing to its low CaO content this belite-type Roman cement liberates less Ca(OH)<sub>2</sub> on hydration than a Portland cement of the alite-type which is sintered almost at the point of fusion of the cement mixture.

The mechanical properties and compositions of Roman mortar and concrete [117] under exposure to spring, sea and mineral-spring waters are summarized in Tables 17 and 18. Roman cements made in earlier periods and not ground to present-day standards of fineness, as well as the concretes made with them, proved highly resistant even in very aggressive ground-water.

The lime concrete and plaster-mortar in all ancient hydraulic structures described show good durability under various aggressive conditions - flowing fresh water, sea-shore air, sea water and waves, and hot mineral-spring water. No sulphate attack failure due to sea water were observed in the Roman concrete and mortar [60, 117].

TABLE 17 - PROPERTIES OF AGGREGATES USED AND MIXTURE PROPORTIONS OF MORTARS [Ref. 117]

N°	Type of mortar	Locality	Size of aggregates [mm]		Thickness of binder cover of the sand [mm]	Mixture proportion (by Volume)				
			Sand	Coarse		Binder (CaCO <sub>3</sub> )	Sand	Coarse aggregate	Terra cotta	Charcoal
1	Gray concrete mortar	Aqueduct Caesarea	0,5	5	0,1	1	1,5	—		0,5
2	Reddish plaster mortar	Aqueduct Caesarea	0,5	3	0,05	1	1,0	—	10	—
3	White concrete mortar	Quay, Tiberias	2	10	0,05	1	1	3	0,25	—
4	White concrete mortar containing tuff	Seashore, Caesarea	0,5	30	0,1	1	1	Tuff 3		
5	White concrete mortar containing basalt aggr.	Hot Springs, Tiberias	2	10	0,05	1	1	3,5		

TABLE 18 - PROPERTIES OF ROMAN MORTARS [Ref. 117]

N°	Type of mortar	Locality	Type of water	Unit weight dry [kg/m <sup>3</sup> ]	Maximum water absorpt. (Porosity) %	Compressive strength [kg/cm <sup>2</sup> (Schmidt hammer)]	
						mortar	stone
1	Gray concrete mortar	Aqueduct, Caesarea	Fresh spring	1500	35—40	60	~400
2	Reddish plaster mortar	Aqueduct Caesarea	Fresh spring	1850	15	300	400
3	White concrete mortar	Quay, Tiberias	Fresh lake	2150	20	200 120	~800
4	White concrete mortar containing tuff	Seashore, Caesarea	Mediterranean sea	1650	26	120	—
5	White concrete mortar containing basalt aggr.	Hot Springs, Tiberias	Mineral spring	2340	8 16	250 150*	800

\*) Near water.

## 6. LONG-TERM STABILITY OF CONCRETE

Concrete durability will depend on the following factors:

- Chemical and electrochemical compatibility with the host rock. This eliminates reactions which could adversely affect the stability of the concrete in the repository site.
- Chemical and physical stability in the in-situ repository environment. The concrete should not be adversely disintegrated by groundwater, pressure or temperature. Additionally, the concrete should be thermodynamically stable so that its ability to withstand environmental stresses and perform adequately is not altered over very long time periods.

### 6.1 THE INFLUENCE OF CHEMICAL CHANGE

Many concrete structures exposed to highly aggressive media for prolonged periods of time have withstood such exposures successfully without any special protective measures. Dense concrete is one of the essential prerequisites of sulphate resistance even when using cements of low  $C_3A$  content.

The combined corrosive effect of several factors is to be expected in the case of the concrete structure surrounded by:

- groundwater
- clay, quartz or bentonite-based buffering materials which have some ion exchange capability
- radiation due to the radwaste
- high pressure
- high temperature.

The major constituent of hydrated cement paste is C-S-H which is considered to be thermodynamically metastable with respect to crystalline calcium silicate hydrates of the same composition. With prolonged time the metastable constituents will crystallize and porosity will be increased very slightly at 100°C.

Increased porosity of 1-2% by volume is partly caused by conversion of the various metastable hydrated calcium aluminate phases normally found at room temperature to the stable, but weaker cubic hydrates.

A maximum stability temperature of  $105 \pm 5^\circ\text{C}$  at elevated water pressures in the range of 690-1380 kPa has been established for the reversibility of the reaction: ettringite  $\rightleftharpoons$  calcium monosulphoaluminate hydrate + calcium sulphate hydrate. This sets an upper temperature limit at modest water pressures for the effectiveness of ettringite as a phase giving rise to expansion for tightening the structure.

Micromorphological features of the interfacial zone between cement paste and wall rock include formation of a duplex film on the rock surface, development of large well-formed  $\text{Ca}(\text{OH})_2$  crystals at intervals near the interface, development of stacked-platelet secondary  $\text{Ca}(\text{OH})_2$  in open spaces immediately adjacent the duplex film, and hydration leading to the presence of hollow-shell hydration grains in the interfacial region.

The exceptionally high mechanical properties of high pressure- and temperature-cured concretes are attributed to a strong chemical bond between cement matrix and aggregate.

#### 6.1.1 THE PERIOD OF 0-100 YEARS

No damage would be made by chemical change over fifty years as shown in Section 5.6. Carbonation rate will be very low since the concrete is saturated under humid conditions. Carbonation increases slightly the strength of concrete based on Portland cement and depth of carbonation would be around 50 mm for good concrete over 100 years.

In a concrete permeated by aggressive groundwater, the question whether automatic sealing occurs, or seepage assumes detrimental proportions depends on the degree of permeability. In fact, seepage usually results in spontaneous sealing - in spite of the leaching of some readily soluble cement components - as long as the loss of material is offset by internal swelling.

Assuming that the host rock has about 0.5 percent porosity as it is in much of the bedrock, concrete of 10-20 mm thickness would be attacked by sulphate diffusion during the period of 100 years because of the corrosive-inhibitive effect of  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  ions in the groundwater. A remarkably high resistance can be obtained by the careful composition and proper compaction of concrete.

The  $\text{Cl}^-$ , in the early stage of immersion, shows very fast and deep penetration into the concrete as compared to  $\text{SO}_4^{2-}$ ;  $\text{Cl}^-$  reacts in this case with  $\text{Ca}(\text{OH})_2$  to convert  $\text{Ca}^{2+}$  into an extractable species in aqueous phase and hence to make the specimen slightly porous, although most of the  $\text{Cl}^-$  is retained in the concrete as Friedel's salt ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Ca}(\text{Cl}_2, \text{SO}_4) \cdot 12\text{H}_2\text{O}$ ). The  $\text{SO}_4^{2-}$  in the later stage shows slow penetration into the concrete; the  $\text{SO}_4^{2-}$  which impregnates through the surface layer of the concrete reacts with the Friedel's salt to form ettringite.

#### 6.1.2 THE PERIOD OF $10^2$ - $10^4$ YEARS

The behaviour of crystalline phase designated C-S-H in the concrete under high temperature and pressure over extremely long periods of time is uncertain and in a repository where the initial temperatures are elevated a certain number of reaction products created can determine the long-term stability. There is a possibility that deleterious effects resulting in increased permeability may accompany recrystallization of the metastable phase.

Porosity would increase up to 3-3.5 percent by volume and it is not known whether internal microcracks will be created by this increased porosity.

The formation of quantitative criteria for the degree of aggressivity is a very difficult task. In the worst case, sulphate attack would be around 100 mm thickness over 1,000 years, whilst 500 mm thickness would be affected by sulphate aggression over 10,000 years.  $\text{Ca}(\text{OH})_2$  leaching by concentration gradient would be about 5 mm over 1,000 years and 15 mm over 10,000 years. Magnesium exchange would be the similar order of magnitude.

Some partially recrystallized pozzolanic cements such as from ancient Roman concrete have shown durability for more than 2,000 years. Antique construction based on Roman cement has the following features:

- $\text{Ca(OH)}_2$ -content is much lower than in modern concrete
- it is assumed that Roman concrete has only  $\text{C}_2\text{S}$  since firing temperature have not exceeded 1000-1100°C ( $\text{C}_2\text{S}$  and  $\text{C}_3\text{S}$  are formed at the temperatures of 900°C and 1450°C, respectively).

The low tricalcium aluminate content of the Roman cement increases its resistance to sulphate attack; pozzolans increase also the resistance to other forms of chemical attack such as the leaching of hydrated lime and reduce their permeability.

## 6.2 STRUCTURAL BEHAVIOUR

The time-dependent structural behaviour of hardened concrete at the microscopic level, is characteristic of heterogeneous, anisotropic multi-phase materials. The time-dependent deformations caused by applied loading or by temperature can be attributed mainly to processes which occur in the spaces between the colloidal crystalline particles of the gel matrix due to the diffusion of the confined liquid. Unrecoverable inelastic deformations are attributed mainly to the tendency of the metastable gel system, with its enormous surface energy towards increased stability with time.

The volume changes of concrete with change in moisture content are inherent characteristics of hydraulic cement concrete. It is the change in moisture content of the cement paste that causes the shrinkage or swelling of concrete, whilst the aggregate provides an internal restraint which significantly reduces the magnitude of these volume changes.

### 6.2.1 THE PERIOD OF 0-100 YEARS

Since carbon dioxide does not penetrate deep into the mass of concrete, shrinkage due to carbonation is of minor importance in the overall shrinkage of a concrete structure in humid conditions. The overall structure of concrete will expand very slowly because of swelling of concrete due to immersion in the water. Reversible swelling would be about two-thirds of the initial shrinkage of concrete. Continuous swelling was observed over six years in the case of cement paste. The swelling of concrete would be about 0.15 per mil over 100 years. Swelling can produce a good fit in confined areas and it has self-healing effects.

After 30 years the concrete still creeps continuously. Creep increases with temperature and it appears to be 2-3 times higher at 100°C compared with that of concrete at room temperature. Since creep deformation would be around 0.02 per mil over 100 years, no risk will be expected from small creep changes. Permeability would be about 150 percent of the initial value measured at room temperature, due to the reduction of specific surface by the elevated temperature. By the end of 100 years, the relaxation of major parameters will occur in the concrete structure.

### 6.2.2 THE PERIOD OF $10^2$ - $10^4$ YEARS

Continuous swelling of concrete emerged in water would be about  $100$ - $120 \times 10^{-6}$  over 1,000 years. Thermal expansion of the concrete would be compatible with that of the host rock to control development of thermally induced stresses. It probably is desirable to maintain stresses in the concrete in a compression range to minimise the potential for cracking.

Creep deformation would be around  $130 \times 10^{-6}$  over 1,000 years and this deformation may increase up to 2-3 fold at high temperatures. The real creep may be less due to the crystal growth by recrystallization. Internal stress may not be created by the extremely slow crystallization. After the thermal period of several hundred years at the repository site the temperature will decrease gradually and creep will be even smaller due to the very much lower temperature gradient.

### 6.3 MECHANICAL INTEGRITY

The concrete must be durable enough to maintain the integrity of the structure for very long time periods. Cracks are normally caused by stresses that develop in concrete due to the restraint of volumetric change or to loads which are applied to the structure. The magnitude of cracking during drying of the concrete is influenced by a combination of factors, such as (a) the amount of shrinkage, (b) the degree of restraint, (c) the modulus of elasticity of the concrete, and (d) the creep or relaxation of the concrete.

#### 6.3.1 THE PERIOD OF 0-100 YEARS

Concrete which has the required strength can be expected to last very long period of time, and the cement content should be kept low to minimize heat generation and resultant potential cracking. A multilayer structure is better to avoid thermally induced cracking during crystallization. Stress induced crackings can occur in the case where expansion coefficients of cement paste and aggregates are different. Autogeneous healing would be possible due to the continuous hydration and crystallization.

The surface cracks of structural concrete [104] are very narrow, a total crack width =  $\Delta T.L.10^{-5}$  is commonly measured. Crack formation would not occur if correct choice of materials, optimum mix formulation and well compacted concretes are used in the repository environment. The thermal expansion of surrounding rock is smaller than that of concrete, which can give a self-healing effect.

Deformation of the tunnel dome can provoke cracks in the rock. Structural concrete with good strength can prevent this effect. If the supporting strength is high enough, backfilling materials with low strength can be used for keeping canisters or drums in place.

### 6.3.2 THE PERIOD OF $10^2$ - $10^4$ YEARS

Cracks can be controlled by correct construction practices. The initial integrity of concrete immersed in groundwater will gradually diminish due to the corrosive nature of groundwater, high pressure and temperature. Adequate strength appears to be maintained during the period of sulphate attack and subsequent leaching. The rate of groundwater flow and the ion exchange potential of the repository rock seem to be important factors in ensuring the mechanical integrity of structural concrete.

## 6.4 REINFORCEMENT

A series of bond pull-out tests has been carried out at Oak Ridge National Laboratory to determine the effect of elevated temperatures up to 149°C on the bond strength between concrete and steel reinforcement. It would appear that a bond strength equal to 85 percent of the room temperature value could be used in designing a foundation to operate under temperatures ranging from 24°C to 149°C.

### 6.4.1 THE PERIOD OF 0-100 YEARS

Corrosion is promoted by carbonation, which reduces the alkalinity of concrete. In concrete of good quality, properly compacted and cured, carbonation will penetrate to a small depth only, as discussed in Section 6.1.2. If reinforcement is employed for structural concrete, surface cracking would be very narrow. If the crack formation is wider than 0.1 mm, then the corrosion will be accelerated.

Acting as an electrolyte in concrete, chlorides may bring about a major corrosion of the reinforcement. The detrimental effect is limited as long as the concrete is sufficiently dense and the reinforcement covered with 50 mm-thick concrete.

In moist concrete, the reinforcing steel is usually protected from corrosion by a thin oxide film coating on the surface as shown in Section 3.4. The formation and preservation of this layer depend essentially on the structure and thickness of the concrete cover. Once the oxide layer is destroyed by chlorides, the steel will corrode at a great rate.

### 6.4.2 THE PERIOD OF $10^2$ - $10^4$ YEARS

All the reinforcement would be corroded within several hundred years. The problems of protecting reinforcement against aggressive chloride attack or of keeping damages to concrete structures within tolerable limits are rather complex. The factors controlling the chemical resistance of reinforcement are, in spite of a vast volume of research, still little understood. The life of reinforcement could be prolonged to some extent with additional protection such as epoxy coating or the use of more corrosion resistant alloys for the reinforcement.

## 7. CEMENT COMPOSITION FOR SOLIDIFICATION OF RADWASTE

For many years concrete has been considered for, or used for immobilization of low-level and intermediate-level radioactive wastes [118-131]. Concrete is considered attractive because the raw materials are inexpensive, only ambient temperatures are required, and processing operations are relatively simple. Cement for radwaste should be stable not only thermally but also chemically and mechanically throughout the extended time framework.

### 7.1 TYPE OF WASTE INCORPORATED IN CONCRETE

Low-level radwaste and intermediate-level radwaste are usually liquid concentrates and solid waste generated as by-products of the liquid radwaste treatment systems in nuclear power plant. Wet solid wastes constitute the major solid waste on an activity basis and can be classified into four basic types:

- spent resins
- filters and sludges
- evaporator concentrates
- miscellaneous liquids.

The solidification of high-level defence radioactive waste in concrete has been investigated by Savannah River Laboratory [132] and Brookhaven National Laboratory [133], whilst studies on fixation of reprocessing waste containing actinide elements have been conducted by Hanford Engineering Development Laboratories [121]. Other types of radioactive wastes considered for solidification in concrete include Redox [134] and Purex sludges [135], aqueous and solid sodium nitrate waste [136,137], various solid calcines [138], tritium [139], radioactive iodine [140] and solids loaded with krypton-85 [141]. The advantages and usage of concrete for solidification of these waste types suggest the possibility of incorporating high specific activity wastes in concrete.

## 7.2 CEMENT/WASTE COMPOSITE

(Comment on mix formulation supplied by EIR)

An optimum mix formulation (Table 19) for solidification of concentrated radioactive waste solution containing 15%  $H_3BO_3$  and some properties of radwaste concrete (Table 20) have been supplied by EIR (Swiss Federal Institute for Reactor Research). This formulation will be briefly commented from the standpoint of the cementing mechanism for compatibility with radioactive waste and long-term stability. Since it has been indicated by Dr. Laske and his coworkers [142-150] at EIR that HTS cement (supplied by Ciments Lafarge SA) and Sulfacem (supplied by Portlandcementwerk A.G., Olten) have shown better results compared with the other cements, these two cements have been chosen for the purpose of discussion. Chemical and mineralogical analyses of HTS and Sulfacem cements are given in Table 21.

TABLE 19 - MIX-FORMULATION FOR SOLIDIFICATION OF RADWASTE  
[Ref. 142]

100 parts	HTS sulphate resisting cement
30 parts	Trass
20 parts	Hydrated lime
72 parts	Concentrated radwaste solution containing 15% $H_3BO_3$
Water-Cement ratio:	0.61

TABLE 20 - PROPERTIES OF RADWASTE CONCRETE [Ref. 150]

Wet density	1.89 g/cm <sup>3</sup>
Porosity	30% (by volume)
Compressive strength	45 N/mm <sup>2</sup>
Water resistance	good at 70°C good at 80°C
Sulphate resistance	good
Bulk leach rate	
distilled water	Cs: $1 \times 10^{-4}$ g/cm <sup>2</sup> day Co: $3-7 \times 10^{-6}$ g/cm <sup>2</sup> day
saturated CaSO <sub>4</sub> solution	Cs: $7 \times 10^{-6}$ g/cm <sup>2</sup> day Co: $3-7 \times 10^{-6}$ g/cm <sup>2</sup> day

TABLE 21 - CHEMICAL ANALYSES OF SULPHATE RESISTING CEMENTS

Chemical and mineralogical component	HTS (Lafarge) %	Sulfacem (Olten) %
SiO <sub>2</sub>	24.05	20-21
Al <sub>2</sub> O <sub>3</sub>	2.57	2.8-4.2
Fe <sub>2</sub> O <sub>3</sub>	1.49	7-7.5
CaO	67.86	62-63
MgO	0.70	-
SO <sub>3</sub>	2.06	-
CO <sub>2</sub>	0.25	-
H <sub>2</sub> O	0.50	-
K <sub>2</sub> O	0.16	-
Na <sub>2</sub> O	0.10	-
Free CaO	0.58	-
Insolubles	0.09	-
C <sub>3</sub> S	64.90	45-50
C <sub>2</sub> S	20.10	20-22
C <sub>3</sub> A	4.29	0
C <sub>4</sub> AF	4.50	18-20
C <sub>2</sub> F	-	0-2

### 7.2.1 CHEMICAL STABILITY

Under the anticipated environmental conditions in Switzerland it is desirable to use a sulphate resistant cement for long-term chemical and thermal stability when incorporating high concentration of certain radioactive waste species. The addition of waste to cement-water mixtures has been shown to influence set time. A decrease of set time can sometimes be attributed to the heat of hydration of the waste components.

Borate wastes and boric acid from the reactor coolant can prevent cement paste from setting if used in sufficient quantities. In order to improve the hydration and setting characteristics of these waste forms lime is added to borate waste/cement paste, as shown in Table 19. Boric acid also decreases the rate of heat release and the total heat liberated during the curing of concrete, whilst calcium hydroxide has the opposite effect on curing exotherms when used with boric acid.

As discussed in Section 3.3.1 the content of  $C_3A$  is very important factor to control the chemical resistance. The  $C_3A$  content of sulphate resisting cement should not exceed 5.4 percent. One method of increasing the sulphate resistance is the substitution of the compound  $C_3AF$  for  $C_3A$ . However, too high a content of  $C_4AF$  decreases the chemical resistance of low- $C_3A$  contents and Sulfacem appears to have very high content of  $C_4AF$ . The ASTM specification limits the  $C_4AF$  content by placing a maximum of 20 percent on the sum of the  $C_4AF$  plus twice the  $C_3A$  content.

### 7.2.2 MECHANICAL STABILITY

Compressive strengths of cement-sludge samples progressively decrease with increasing waste content; the decreases are primarily due to the lack of strength of the sludge particles. Fractography indicates that fracture originates at the surface of the sludge particles; this implies that the irregular interface between agglomerates and the cement matrix acts as a stress concentrator. Trass (a volcanic ash pozzolana) used as a sorbent

for reducing leachability tends to decrease strength; however, formulations with sludge plus sorbent exhibit strengths that are higher than those of formulations with sludge or sorbent alone.

The strength of concrete waste forms is an important parameter in safety and accident evaluations. The composite must exhibit sufficient strength to withstand handling, transportation, and possible accident situations without major damage. Current regulations, however, do not specify a minimum compressive strength requirement for radwaste/cement composites. Since it is suggested in the literature [151] that the minimum crushing strength of a radwaste concrete should be  $5 \text{ N/mm}^{-2}$ , compressive strength of  $45 \text{ N/mm}^{-2}$  obtained by an optimum mix formulation at EIR is sufficiently high.

### 7.2.3 LEACHABILITY

Leachability is considered a very important parameter in the safety evaluation of radioactive waste forms. Under normal conditions the waste forms would be contained within sealed drums. Leachability becomes a concern under geologic repository situations where the container is breached and water is allowed to come in direct contact with the waste form.

Cesium, strontium, and alpha emitters are the species of greatest concern in radioactive waste solidification and have received the largest attention concerning their leachability. Another species in cement/waste composites that has been leach tested is sodium nitrate.

Leachability varies with types of cement and sludges. Long cure times and irradiation tend to decrease leachability while prolonged exposure to high temperatures and increased leachant renewal frequency tend to increase leachability.

As shown in Table 20, leachability of cesium is generally greater than that of cobalt from similar waste forms. This difference [152] may be partially explained by mixtures of Portland cement and radioactive liquid solutions, which indicate that leachability is lower for divalent species (Co, Cd) than for monovalent species (Na, Cs).

Cesium leachability values for concrete waste forms suggest that cesium release from the composite is diffusion controlled. Cesium leachability is lower for concrete waste forms with near theoretical water-cement ratios than mixtures with excess water and/or chemical additives such as boric acid.

The rate-determining step of leaching under static conditions is the external diffusion of the species through the interface layer between the solid waste form and the liquid, whilst the rate-controlling step of leaching under dynamic conditions is the internal diffusion of the species through the cement matrix. Bulk leach rates shown in Table 20 appear to be of similar order of magnitude compared with the other researchers' experimental results. The lower leachability of cesium in HTS radwaste cement compared with Sulfacem cement seems to be due to the more rapid development of a dense structure in a high  $C_3S$  cement. HTS cement appears to be compatible with the radioactive waste based on a concentrated solution containing 15%  $H_3BO_3$  and the radwaste cement concrete seems to be stable not only chemically but also mechanically, although a straightforward comparison of the composite properties is difficult, due to the lack of standardized testing procedures.

There appears to be a possibility for improving the quality of radwaste concrete by utilizing admixtures and additives such as grundite which has a high retention capacity for cesium. Overall leachability of concrete waste forms can be reduced considerably by impregnating the interconnecting porosity with monomer, which is subsequently polymerised in situ. Polymer-impregnated concretes exhibit bulk leach rates at least two orders of magnitude lower than cement concrete waste forms [153].

8.

CONCLUSIONS

Concrete that was properly made by the ancient Greeks and Romans is still in excellent condition after 2000 years. Some of the concretes made in this era still contain some unreacted lime which attests to the impermeability of this material to the environment. Concretes used as seawalls have also been found in excellent condition although the leachable calcium fraction was found to have been replaced by magnesium. Although seawall concrete is structurally sound, it is certainly not impermeable to groundwater. Not all concrete has performed as well as the Grecian and Roman concretes during the course of history. In the last fifty years, however, the chemistry of concrete has become sufficiently well understood for producing high quality concretes.

Concrete appears to be a suitable material for structural, filling and sealing applications in the repository environment because of its properties of low permeability, high mechanical strength and the potential for long time chemical, physical and mechanical stability. Concrete can be cemented to ensure the integrity of the whole repository system and good interstitial bonding is formed with the host rock wall. The overall requirement for the stability of concrete is chemical and electrochemical compatibility and thermodynamic equilibrium with the surrounding formation.

The following conclusions are general consideration for the selection of materials and recommended practices to ensure maximum durability of cement and concrete for nuclear waste disposal:

- A sulphate-resisting (SR) cement should be used to reduce substantially the chemical attack of groundwater.
- The SR-cement should have a relatively high  $C_2S$  content and low alkali content, with less than 0.60% ( $N_2O + K_2O$ ).
- The tricalcium aluminate in the cement should be as low as possible in order to achieve maximum durability of the concrete, but not so low as to diminish its ability to passivate the steel in the presence of chlorides.

- The shrinkage and heat of hydration of a SR-cement should be avoided, which may cause cracks.
- Aggregates ought to be non-reactive and sound, and to have low permeability. (Aggregates should be selected from a satisfactory past history of durability in groundwater or seawater).
- Thermal mis-match between aggregates and cement matrices should be avoided to reduce the risk of thermally induced cracks.
- Water-cement ratio: to be as low as possible and preferably 0.40 or less.
- The amount of chlorides and sulphates in the mix should be reduced to a minimum.
  - a) mixing water:  $\text{Cl}^-$  less than 500 ppm  
 $\text{SO}_4^{2-}$  less than 1000 ppm
  - b) aggregates:  $\text{Cl}^-$  less than 0.02 wt%
  - c) admixtures: not more than 0.25 wt% of chlorides and sulphates (great care is required to select an optimum admixture for specific application).
- Concrete should be a workable mix, well compacted and consolidated by vibration, and free from honeycomb or rock pockets so that a dense, high quality concrete can be produced.
- Concrete cover over reinforcement steel should normally be not less than twice the maximum size of the coarse aggregate or 2.0 times diameter of the reinforcing bar, whichever is greater.
- The placement techniques must be chosen so that a high interstitial bonding between cement and host rock is obtained. Overheating should be avoided otherwise thermal stress cracking and cracking due to cooling might occur. Much of the tensile strain induced by thermal gradients would be relieved by creep in the curing period.

- In establishing the best procedure for placing cement and concrete, many procedures can be envisaged and the final choice should depend upon the result of full scale experiments.
- Concrete offers some advantages as a backfill, protecting the metal overpack from corrosion and providing a very good long-term barrier to groundwater and to unauthorized access, and should therefore be considered along with bentonite for the repository design.

Cement can also be used successfully for the immobilization of low-level, intermediate-level and aged high-level wastes. Advantages of cement include inexpensive raw materials, low processing temperatures and handling simplicity. Concrete waste forms show acceptable thermal, chemical, physical and radiolytical stability.

## 9. SUGGESTIONS FOR FUTURE WORK

Possible further investigations identified can be divided into the five groups as shown below:

1. Experimental study on the combined effect of temperature and pressure on the stability of concrete with and without groundwater.

It would be more relevant to evaluate long-term stability and leachability under the pressure, temperature and chemical environment which is equivalent to the potential repository site. These technical data would provide vital information for predicting more accurately long-term behaviour of cement and concrete used in the repository environment.

2. Effect of admixtures and additives on stability of cement and concrete

Additives and admixtures should be included in the future work to determine their effect on permeability, leachability and long-term durability:

- to reduce early age temperature rise
- to contribute to later age strength gain
- to form more stable and durable calcium silicate hydrates.

High strength, low permeability cements with viscosities and setting properties allowing them to be pumped are required for adequate filling around canisters and drums, and shaft sealing in the repository site.

Additives and admixtures to be considered for modifying properties include:

- accelerators
- retarders
- low density additives
- high density additives
- low water loss additives
- lost circulation materials
- dispersants.

3. Stability of special cements such as geothermal, oilwell and expansive cements.

Geothermal, oilwell and expansive cements appear to be feasible from an overall engineering and economic standpoint for backfillings and sealing shafts and galleries. Hydrothermal cements involve transport and deposition of cementing material at high temperature and pressure. This method can produce concrete which is theoretically durable for very long period of time.

Expansive cement provides a positive expanding force against the rock surface of the repository site after hardening when shrinkage during cooling takes place. This expansive force should reduce the microfractures in the distressed annulus of rock around the structural concrete. It should help achieve a 'tighter' interface between the concrete and the rock to improve bonding resistance to movement and the impermeability of the concrete at the interface.

4. Study on ancient constructions such as Roman concrete found in Liestal-Augst near Basel.

5. Cement formulation for the solidification of radwaste.

When the optimum composition for immobilisation of ion exchange resin (Powdex and Lewatite) is established at EIR, it would be desirable to evaluate the long-term stability of radwaste concrete from the standpoint of the chemistry of cement.

Geneva, March 1982

E7-2225-01/WSS/mf

REFERENCES

- [1] M.D. Hill, "Disposal of radioactive waste", Europhysics News 12(5), 9-11, May 1981.
- [2] B.D. Patterson, S.A. Dave and W.J. O'Connell, "Nuclear waste management: storage and disposal aspects", UCRL-84918, CONF-800904-2, September 1980.
- [3] H.O. Weeren and J.J. Perona, "A preliminary engineering and economic analysis of the fixation of high-level radioactive wastes in concrete", ORNL/TM-6863, Contract No W-7405-eng-26, July 1979.
- [4] J.O. Blomeke, "Management of radioactive wastes", Contract W-7405-eng-26, presented at Seminar at School of Nuclear Engineering, A & M University, College Station, Texas, November 5-9, 1979.
- [5] R.A. Heckman and C. Minichino, "NRC Waste Management Program Reports", UCID 18133, Vol. 1, Lawrence Livermore Laboratory, August 1979.
- [6] A.T. Prince, "Radioactive waste storage and disposal: the challenge", CA-7904-268, Notes for an address at the Canadian Institute of Mining & Metallurgy, Ottawa branch luncheon, March 15, 1978.
- [7] C.S. Fore, N.D. Vaughan and L.K. Hyder, "Low-level radioactive waste technology: a selected, annotated bibliography", Vol. 2, ORNL/EIS-133/V2, Contract No W-7405-eng-26, October 1980.
- [8] G.J. McCarthy, W.B. White, R. Roy, B.E. Scheetz, S. Komarnenz, D.K. Smith and D.M. Roy, "Interactions between nuclear waste and surrounding rock", Nature 273, 216-217, 18 May 1978.
- [9] E. Detilleux, K.D.B. Johnson and P. DeJonghe, "Handling and disposal of high level processed waste", Proc. of Nuclear Power Option for the World, European Nuclear Conference' 79, Foratom VII Congress, 120-123, Hamburg, Germany.

- [10] "Radioactive waste management", Atom 279, 15-17, January 1980.
- [11] F.M. Lee, "The chemistry of cement and concrete", Third Edition, Edward Arnold (publishers) Ltd., 1976.
- [12] D.D. Double and A. Hellowell, Nature 261, 486, 1976.
- [13] D.D. Double, A. Hellowell and S.J. Perry, Proc. Roy. Soc. (London), A 359, 435, 1978.
- [14] J.D. Birchall, A.J. Howard and A.J. Bailey, Proc. Roy. Soc. (London), A 360, 445, 1978.
- [15] L. Dent Glasser, Cem & Concr. Res. 9, 515, 1979.
- [16] D.D. Double, H.L. Thomas and D.A. Jameson, "The hydration of Portland cement", 7th International Congress on the chemistry of cement, II-256, Paris, 1980.
- [17] T.C. Powers, J. Portland Cement Assn. Res. Dev. Labs. 3, 47, 1961.
- [18] J. Skalny, J.F. Young, "Mechanisms of Portland cement hydration", 7th International Congress on the chemistry of cement, II-1/3, Paris, 1980.
- [19] H.F.W. Taylor, D.M. Roy, "Structure and composition of hydrates", ibid, II-2, Paris, 1980.
- [20] R.A. Helmuth, "Structure and rheology of fresh cement paste", ibid, VI-0/16, Paris, 1980.
- [21] S.K. Chopra, "Physical properties and structure of fresh cementitious paste", Symposium on structure of Portland cement paste and concrete, Special Report 90, Highway Research Board, p. 9, 1966.

- [22] S. Diamond, "Cement paste microstructure - an overview at several levels", Proceedings of a conference on hydraulic cement pastes: their structure and properties held at University of Sheffield, 8-9 April, 1976, p. 2, Cement and Concrete Association.
- [23] P.K. Mehta and D. Manmohan, "Pore size distribution and permeability of hardened cement paste". 7th International Congress on the Chemistry of Cement. VII-1, Paris, 1980.
- [24] G.J. Verbeck and R.H. Helmuth, "Structures and physical properties of cement paste", Proceedings of the Fifth International Symposium on the Chemistry of Cement, Tokyo, 1968.
- [25] S. Diamond and W.L. Dolch, "Generalised log-normal distribution of pore sizes in hydrated cement paste", Journal of Colloid and Interface Science 38(1), 234, 1972.
- [26] E.J. Sellevold, "Mercury porosimetry of hardened cement paste cured or stored at 97°C", Cement and Concrete Research 1(3), 399-404, 1974.
- [27] J. Jamber, "Influence of water-cement ratio on the structure and strength of hardened cement paste", Proceedings of a conference held at University of Sheffield, p. 175, April 1976.
- [28] B.K. Nyame and Dr. J.M. Illston, "Capillary pore structure and permeability of hardened cement paste", 7th International Congress on the Chemistry of Cement, VI-181, Paris, 1980.
- [29] A.M. Neville, "Properties of Concrete", 2nd Edition, Pitman Publishing, England, 1975.
- [30] T.C. Powers, L.E. Copeland, J.C. Hayes and H.M. Mann, "Permeability of Portland cement paste", J. Amer. Concrete Institute, p. 285, December 1955.

- [31] L. Struble and J. Skalny, "A review of the cement-aggregate bond", *Cement and Concrete Research* 10, 277-286, 1980.
- [32] G.P. Tognon and S. Cangiano, "Interface phenomena and durability of concrete", 7th International Congress on the Chemistry of Cement, VII-133, Paris, 1980.
- [33] J.C. Maso, "The bond between aggregates and hydrated cement paste", *ibid*, VII-1, Paris, 1980.
- [34] B.D. Barnes, "Morphology of the paste-aggregate interface", Ph.D. Thesis, Purdue University, 1976.
- [35] D.W. Hadley, "The nature of the paste-aggregate interface", Ph.D. Thesis, Purdue University, 1972.
- [36] T.Y. Lyubimova, and E.R. Pirus, "Crystallization structure in the contact zone between aggregate and cement in concrete", *Colloid J. USSR*, 24(5), 491-498, 1962.
- [37] K.M. Alexander, J. Wardlaw and D.J. Gilbert, "Aggregate-cement bond, cement paste strength and the strength of concrete". *Proceedings of an International Conference, The Structure of Concrete*, p. 59-81, Cement and Concrete Association, London, September 1965.
- [38] C.F. Scholer, "The role of mortar-aggregate in the strength of concrete", *Highway Research Rec.* 210, 108-117, 1967.
- [39] O. Valenta, "Durability of concrete", *Fifth International Symposium on the Chemistry of Cement, Tokyo, Vol. III*, 193-225, 1969.
- [40] K. Newman, "The structure and properties of concrete - an introductory review", *Proceedings of an International Conference on the Structure of Concrete, Cement & Concrete Association, London, September 1965*.

- [41] R.K. Dhir, C.M. Sangha and J.G.L. Munday, "Strength and deformation properties of autogenously healed mortars", ACI Journal, p. 231, March 1973.
- [42] J. Callaje, "Durability", 7th International Congress on the Chemistry of Cement, VII-2/1, Paris, 1980.
- [43] L. Patotas, "Theoretical problems concerning the durability of concrete", RILEM International Symposium on Durability of Concrete, pp. 59-78, Prague, 1962.
- [44] D.F. Orchard, Concrete Technology 1, 443, 4th edition, Applied Science Publishers Ltd., 1979.
- [45] A.D. Buck, "Control of reactive carbonate rocks in concrete", Techn. Report C-75-3, U.S. Waterways Experimental Station, 1975.
- [46] M. Hamada, "Carbonation of concrete", Proceedings of the Fifth International Symposium on the Chemistry of Cement, Session III-3, Tokyo, 1968.
- [47] T. Akiba, K. Minegishi and G. Sudoh, "Mechanisms and kinetics on neutralization of concrete in sea water", 7th International Congress on the Chemistry of Cement, VII-57, Paris, 1980.
- [48] R. Tsukayama, H. Abe and S. Nagataki, "Long-term experiments on the neutralisation of concrete mixed with fly ash and the corrosion of reinforcement", *ibid*, IV-30, Paris, 1980.
- [49] P. Longuet and P. Courtault, RILEM Symposium on Concrete Carbonation, (Wexham-Springs, England), Comm. 2.4, 1976.
- [50] A. Meyer, H.J. Wierig and K. Husmann, "Karbonatisierung von Schwerbeton", Deutscher Ausschuss für Stahlbeton, Heft 182, Berlin, 1967.

- [51] T.J. Reading, "Combating sulphate attack in corps of eng. concrete construction", ACI SP-47, 343-366, 1975.
- [52] W. Kobayashi, S. Okabayashi and N. Kataoka, "Study on sulphate resistance of various types of cement", Rev. 28th Gen. Meeting Cem. Assoc. Japan, 78-80, 1974.
- [53] S.K. Chatterji, "Mechanism of sulphate expansion of hardened cement pastes", Proc. V. ISCC (Tokyo) III-138, 336-341, 1969.
- [54] A.M. Naville, "Behaviour of concrete in saturated solutions and weak solutions of magnesium sulphate of calcium chloride", J. of Mat. 4(4), 781-816, 1969.
- [55] M. Regourd, "Cement Research in France", Cem. Res. Prog., 235-258, 1976.
- [56] R. Kondo, M. Satake and H. Ushiyama, "Diffusion of various ions in hardened Portland cement", Rev. 28th Gen. Meeting Cem. Assoc. Japan, 41-43, 1974.
- [57] F. Dutruel and R. Guyader, "Etude de la corrosion des canalisations en béton", Monographie No 7 du CERIB, France, 1975.
- [58] H. Woods, "Durability of concrete construction", ACI Monograph No 4, 1968.
- [59] F.W. Locher, "Influence of chloride and hydrocarbonate on the sulphate attack", Proc. V. ISCC (Tokyo), III-124, 328-335, 1969.
- [60] I. Biczok, "Concrete corrosion and concrete protection" AKademiai Kiado, Budapest, p. 82, 1972.
- [61] O.E. Gjrv, Ø. Vennesland and A.H.S. El-Busaidy, "Diffusion of dissolved oxygen through concrete". NACE, Corrosion 76, Houston, Texas, 1976, 13 p.

- [62] W.P. Kilareski, "Corrosion induced deterioration of reinforced concrete: an overview", *Materials Performance*, March 1980. p. 48.
- [63] E. Schaschl and G.A. Marsh, *Corrosion* 16(9), 461 t, 1980.
- [64] O.E. Gjrv, "Durability of concrete structures in the ocean environment", *FIP Proceedings, Concrete Sea Structures*, FIP, London, pp. 141-145, 1972.
- [65] O.E. Gjvr, "Control of steel corrosion in concrete sea structures", *ACI SP 49-1*, pp. 1-9, 1974.
- [66] O.E. Gjrv, "Durability of reinforced concrete wharves in Norwegian harbours", *Ingenirforlaget A/S, Oslo*, 208 p., 1968.
- [67] O.E. Gjvr, "Concrete in the Oceans", *Marine Science Communications* 1(1), 51-74, 1975.
- [68] G.D. Brunton and W.C. McClain, "Geological criteria for radioactive waste repositories", *Y/OWI/TM-47*, Springfield, Va., National Technical Information Services, November 1977.
- [69] D.A. Waite and W.E. Newcomb, "Integrated geological and environmental site: qualification criteria", *Battelle Memorial Institute Office of Nuclear Waste Isolation Draft Report, ONWI-33*, Columbus, Ohio, USA.
- [70] M. Bresesti, F. Girardi, S. Orlowski and P. Venet, "Radioactive waste disposal in geological formations: research activities of the Commission of European Communities", *Scientific Basis for Nuclear Waste Management 2*, 31-38, 1980, Plenum Press, New York.
- [71] J.H. Peck and J. Briedis, "Site selection for radioactive waste disposal in geologic formations", *Proceedings of the American Power Conference*, Vol. 41, 215, 1970.

- [72] E.L. Draper, "Environmental standards: their implications for a high-level waste repository", Waste Management 79, Proceedings of the Symposium on Waste Management at Tucson, Arizona, Feb. 26-March 1, 1979, p. 405.
- [73] J.E. Gale, O. Quinn, C. Wilson, C. Forster, P.A. Witherspoon and L. Jacobson, "Hydrogeology characteristics of fractured rocks for waste isolation: the Stripa experience", Scientific Basis for Nuclear Waste Management 2, 507-518, Plenum Press, New York, 1980.
- [74] R.A. Deju, "Evaluation of Basalt Flows as a Waste Isolation Medium". Waste Management '79, pp. 183-198. Proceedings of the Symposium on Waste Management at Tucson, Arizona, Feb. 26-March 1, 1979.
- [75] W.P. Freeborn, M. Zolensky, B.E. Scheetz, S. Komarneni, G.T. McCarthy, and W.B. White, "Shale rocks as nuclear waste repositories: hydrothermal reactions with glass, ceramic and spent fuel waste forms", Scientific Basis for Nuclear Waste Management 2, 499-506, Plenum Press, New York, 1980.
- [76] M. d'Alessandro and A. Bonne, "Radioactive waste disposal into a plastic clay formation: probabilities of the geological containment", *ibid*, pp. 711-720, Plenum Press, New York, 1980.
- [77] P.A. Witherspoon, G.R. Wilson, J.C.S. Long, A.O. Dubois, J.E. Gale and M. McPherson, "The role of large-scale permeability measurements in fractured rock and their application of Stripa", *ibid*, pp. 519-525, 1980.
- [78] R.K. Thorpe, "Characterization of discontinuities in the Stripa granite", *ibid*, pp. 527-534, 1980.
- [79] A. McGarr and H.C. Gay, "State of stress in the earth's crust", *Ann. Rev. Earth Planet. Sci.* 6:405, 436, 1978.
- [80] F.A. Donath and L.S. Fruth Jr., "Dependence of strain-rate effects on deformation mechanism and rock type", *J. Geology*, 79, 347-371, 1971.

- [81] F.A. Donath, "Postclosure environmental conditions and waste form stability in a geologic repository for high-level nuclear waste", Nuclear and Chemical Waste Management, 1(2), 103-110, 1980.
- [82] G. Jacks, "Chemistry of some groundwaters in igneous rocks", Nordic Hydrology 4(4), 207-236, 1973.
- [83] P. Fritz, J.F. Barker and J.E. Gale, "Geochemistry, origin and age of groundwater in the Stripa (Sweden) test mine", Scientific Basis for Nuclear Waste Management 2, 543-552, Plenum Press, New York, 1980.
- [84] U. Lindblom, "Groundwater movements around a repository: Phase 1, State of the art and detailed study plan", KBS-TR-06, 28.2.1977.
- [85] "A study of time-related properties of concrete", Project 1016-1B, Engineering Analyses and Tests, E. A & T. Co. Inc., 4676 Admiralty Way, Marina del Rey, Ca. 90291, USA, December 1977.
- [86] T. Soda and K. Yamazaki, "Long-time study on the neutralization of concrete and the rusting of reinforcement in concrete", Japan Cem. Eng. Assoc. Rev. 12th General Meeting, Tokyo, May 1958, pp. 91-93.
- [87] E.B. Nelson and G.L. Kalousek, "Effects of  $\text{Na}_2\text{O}$  on calcium silicate hydrates at elevated temperatures", Cement Concr. Res. 7, 687-694, 1977.
- [88] G.L. Kalousek, "CSH(I)-binder of potentially superior strength", Cement Concr. Res. 6, 417-418, 1976.
- [89] S.O. Oyefesobi and D.M. Roy, "Hydrothermal studies of type V cement-quartz mixes", *ibid*, 6, 803-810, 1976.
- [90] S.O. Oyefesobi and D.M. Roy, "Hydrothermal studies of special types of cement mixed with quartz", *ibid*, 7, 95-102, 1977.

- [91] G.L. Kalousek and E.B. Nelson, "Hydrothermal reactions of dicalcium silicate and silica", *ibid*, 8, 283-290, 1978.
- [92] G. Chiochio, M. Collepardi and R. Turriziani, "Substituted hydrated calcium silicates obtained in autoclave hydration", *J. Am. Ceram. Soc.* 58, 185-188, 1975.
- [93] T. Thorvaldson, "Effect of chemical nature of aggregate on strength of steam-cured Portland cement mortars", *J. Amer. Concr. Inst.* 52, 771-780, 1956.
- [94] G.L. England, "A study of the time-dependent strains in concrete maintained at elevated temperatures and their effects in reinforced concrete", Ph.D. Thesis, University of London, p. 231, 1961.
- [95] G.L. Kalousek, "High-temperature steam curing of concrete at high pressure", Session III-5, Proceedings of the Fifth International Symp. on the Chemistry of Cement, Tokyo, 1968.
- [96] U. Schneider, "Bond behaviour & bond strength at high temperatures", *Betonwerk + Fertigteil Technik, HEFT*, 6, 351-359, 1980.
- [97] H.G. Geymayer, "The effect of temperature on creep of concrete", U.S. Army Engineer Waterways Experiment Station, Corps of Engineers, Vicksburg, Mississippi, AD-699-825, C-70-1, 1970.
- [98] D.M. Roy and A.M. Johnson, "Investigations of stability of calcium silicates at elevated temperatures and pressures", *Proc. of Conf. on Calcium Silicate Building Products, SCI, London, Study of Chemical Industries*, pp. 114-121, 1967.
- [99] C.A. Langston and D.M. Roy, "Morphology and microstructure of cement paste-rock interfacial regions", 7th International Congress on the Chemistry of Cement, VII-127, Paris, 1980.

- [100] C.A. Langton, M.W. Grutzeck and D.M. Roy, "Chemical and physical properties of the interfacial region formed between unreactive aggregate and hydrothermally cured cement", *Cement Concr. Research* 10. 449-454, 1980.
- [101] C.A. Langton, E.L. White, M.W. Grutzeck, and D.M. Roy, "High temperature cements with geothermal applications", 7th International Congress on the Chemistry of Cements, V-145, Paris, 1980.
- [102] O. Valenta, "Durability of Concrete", *Proceedings of the Fifth International Symposium on the Chemistry of Cement*, III-2, Tokyo, 1968.
- [103] H.K. Hilsdorf, J. Kropp and H.J. Koch, "Der Einfluss radioaktiver Strahlung auf die mechanischen Eigenschaften von Beton", *Deutscher Ausschuss für Stahlbeton*, HEFT 261, Berlin, 1966.
- [104] S.G. Bergstöm, G. Fagerlund and L. Romben, "Judgement of properties and function of concrete in connection with final disposal of nuclear fuel wastes in rock". *KBS-TR12*, 77-06-22, 1977.
- [105] G.W. Washa and K.F. Wendt, "Fifty year properties of concrete", *ACI Journal*, Title No 71-4, 20-28, January 1975.
- [106] M.O. Withey, "Fifty year compression test of concrete", *JACI Proc.* 58(6), 695-713, December 1961.
- [107] V.K. Watz, "Festigkeitsentwicklung von Beton bis zum Alter von 30 und 50 Jahren", *Beton*, 3, 95-98, 1976.
- [108] V.K. Walz, "Festigkeitsentwicklung von Beton bis zum Alter von 30 to 50 Jahren", *Beton* 4, 135-138, 1976.
- [109] R. Springenschmid, "Über die Dauerhaftigkeit von Bauwerken aus Beton und Stahlbeton", *Zement und Beton*, 21, 224-229, Heft 5, 1976.

- [110] J.L. Beaton and R.F. Stratfull, "Environmental influence on corrosion of reinforcing in concrete bridge substructures", Highway Research Record 14, 60-78, 1963.
- [111] B.H. Sinn, "Beton gibt es seit 7600 Jahren", Beton 9, 385-385, 1973
- [112] N. Davey, "Building materials in antiquity", Chemy Ind. 43, 1950; A history building materials, Phoenix House, London, 1960.
- [113] F. Ferrari, "Historic review of the use of hydraulic cements", Il Cemento 68(763), 147-150, 1968.
- [114] Faujas de Saint-Fond, "Recherches sur la pozzolane, sur la théorie de la chaux et sur la cause de la dureté du mortier", Grenoble and Paris, 1978.
- [115] C. Hall, "On the history of Portland cement after 150 years", J. Chem. Educ. 53(4), 222-223, 1976.
- [116] R.W. Steiger and M.K. Hurd, "The durability of Concrete". Concrete Construction 25(1), 35-39, January 1980.
- [117] R.M.A. Slatkine and M.B. Yair, "Durability of Roman mortars and concretes for hydraulic structures at Caesarea and Tiberias", RILEM International Symposium on Durability of Concrete, Final Report, 531-544, Prague, 1962.
- [118] R.W. Burns, "Solidification of low- and intermediate-level wastes", Atomic Energy Review 9, 547-599, 1971.
- [119] J.H. Leonard and K.A. Gablin, "Leachability evaluation of radwaste solidified with various agents", Paper 74-WA/NE-8 presented at ASME Winter Annual Meeting, New York, November 17-22, 1974.
- [120] H.W. Heacock and J.W. Riches, "Waste solidification-cement or urea formaldehyde", Paper 74-WA/NE-9 presented at ASME Winter Annual Meeting, New York, November 17-22, 1974.

- [121] Commercial Alpha Waste Program Quarterly Progress Report, October-December 1974, compiled by C.R. Cooley, HEDL-TME 74-41, Hanford Engineering Development Laboratory, Richland, Wa., 1975.
- [122] L.A. Emelity, J.R. Buchholz, and P.E. McGinnis, "Review of radioactive liquid waste management at Los Alamos, LA-UR-77-1195, Los Alamos Scientific Lab., NM, 1977.
- [123] B. Mandahl, B. Persson and C.E. Wikdahl, "Handling of waste at Swedish nuclear plants", IAEA-CM-36-282, International Atomic Energy Agency, Vienna, Austria, 1977 (Conf. 770505-217).
- [124] L.M. Mergan, M. Vandorpe and H. Van de Voorde, "Evaluation of solidification matrices proposed for nuclear power plant radwaste", IAEA-CN-36-186, International Atomic Energy Agency, Vienna, Austria, 1977 (Conf. 770505-217).
- [125] R.M. Neilson Jr. and P. Colombo, "Solidification of liquid concentrate and solid waste generated as by-products of the liquid radwaste treatment systems in light-water reactors", BNL-NUREG-22839, Brookhaven National Lab., Upton, NY, 1977.
- [126] P. Colombo and R.M. Nielson Jr., "Properties of radioactive wastes and waste containers", Quarterly Progress Report, October-December 1976, BNL-NUREG-50664, Brockhaven National Lab., Upton, NY, April 1977.
- [127] J.G. Moore, H.W. Godbee, A.H. Kibbey and D.S. Joy, "Development of cementitious grouts for the incorporation of radioactive wastes, Part 1, Leach studies", ORNL-4962, Oak Ridge National Lab, TN, April 1975.
- [128] D.J. Brown, D.J. Lee, J.D. Palmer, D.L. Smith and A.T.S. Walker, "Cement radwaste solidification studies", First Annual Report, FPC/RWM (80) p. 14, Technology Branch AEE Winfrith, February 1980.

- [129] J.W. Wald, R.O. Lokken, J.W. Shade and J.M. Rusin, "Comparative waste forms study", PNL-3516, UC-70, Battelle Pacific Northwest Laboratory, December 1980.
- [130] C.P. McGinnis and D.A. Housley, "Solid waste disposal study", UCC-ND-08-13-80, Union Carbide Corporation, May 1980.
- [131] D.M. Roy, B.E. Scheetz, L.D. Wakeley and S.D. Atkinson, "Low-temperature ceramic radioactive waste form characterization of supercalcine-based monazite-cement composites", DOE/ET/41900-1, Nuclear Waste Management UC-70, Rockwell International, April 1980 (Contract: DE-AC09-79ET 41900).
- [132] J.A. Stone, "Evaluation of concrete as a matrix for solidification of Savannah River Plant Waste", DP-1448, Savannah River Lab., Aiken, SC, June 1977.
- [133] P. Colombo and R.M. Neilson Jr., "Some techniques for the solidification of radioactive wastes in concrete", Nuclear Technology 32, 30-39, January 1977.
- [134] J.S. Kounts, Ed., Atlantic Richfield Hanford Company Quarterly Report, Technology Development for Long-Term Management of Hanford High-Level Waste, July-September 1975, ARH-ST-132A, Atlantic Richfield Hanford Co., Richland, Wa., 1976.
- [135] J.S. Kounts, Ed., Atlantic Richfield Hanford Company Quarterly Report, Technology Development for Long-Term Management of Hanford High-Level Waste, January-March, 1976, ARH-ST-132C, Atlantic Richfield Hanford Co., Richland, Wa., 1976.
- [136] P. Colombo, "Development of durable long-term radioactive waste composite materials", Progress Report No 10, January-March 1975, BNL-20009, Brookhaven National Lab., Upton NY, April 1975.

- [137] Development of Durable Long-Term Radioactive Waste Composite Materials, Progress Report No 6, January-March 1974, BNL-18830, Brookhaven National Labs., Upton, NY, April 1974.
- [138] Quarterly Progress Report, Research & Development Activities, Waste Fixation Program, April-June 1974, BNWL-1841, Battelle Pacific Northwest Laboratories, Richland, Wa., July 1974.
- [139] R.M. Neilson Jr. and P. Colombo, "Immobilization of tritiated aqueous waste in polymer-impregnated concrete", Trans. Am. Nucl. Soc. 26, 290, June 1977.
- [140] W.E. Clark, "The isolation of radioiodine with Portland cement, Part 1: Scoping leach studies", Nucl. Technol. 36, 215-221, December 1977.
- [141] R.W. Benedict, "An evaluation of methods for immobilizing solids loaded with krypton-85", ICP-1130, Idaho National Engineering Laboratory, Idaho Falls, Id., August 1977.
- [142] D. Laske, "Evaluation of Kd-values by the absorption of cesium and strontium on possible additives in mineral solidifications", NEA-Workshop on Intermediate Level Waste Management, London, May 14-16, 1980.
- [143] W. Hübner, "Versuche zur Verfestigung schwach- und mittel-aktiver Abfälle mit mineralischen Bindemitteln im Hinblick auf eine Endlagerung in geologischen Formationen der Schweiz: 1 Teil: Der Rahmen für die ersten Untersuchungsreihen", TM-CH-192, Eidgenössisches Institut für Reaktorforschung, July 1978.
- [144] W. Hüber, "Versuche zur Verfestigung schwach- und mittel-aktiver Abfälle mit mineralischen Bindemitteln im Hinblick auf eine Endlagerung in geologischen Formationen der Schweiz, 2 Teil: Verfestigungen mit Zementen", TM-CH-211, Eidgenössisches Institut für Reaktorforschung, April 1979.

- [145] W. Hüber, "Versuche zur Verfestigung schwach- und mittel- aktiver Abfälle mit mineralischen Bindemitteln im Hinblick auf eine Endlagerung in geologischen Formationen der Schweiz, 3 Teil: Verfestigungen Borsäure-haltiger Konzentrate mit Zementen", TM-CH-218, Eidgenössisches Institut für Reaktorforschung, June 1979.
- [146] W. Hübner and D. Laske, "Versuche zur Verfestigung Schwach- und mittel aktiver Abfälle mit mineralischen Bindemitteln im Hinblick auf eine Endlagerung in geologischen Formationen der Schweiz, 4 Teil: Prüfung und Untersuchung des Auslagverhaltens der aktiven Zementverfestigungen von Borsäure-haltigen Konzentrat aus dem KKW Beznau", TM-44-80-1, Eidgenössisches Institut für Reaktorforschung, January 1980.
- [147] W. Hübner and D. Laske, "Versuche zur Verfestigung Schwach- und mittel aktiver Abfälle mit mineralischen Bindemitteln im Hinblick auf eine Endlagerung in geologischen Formationen der Schweiz, 5 Teil: Untersuchung des Auslagverhaltens aktiver Zementverfestigungen von Powdex-Ionenaustauschharzen aus dem KKW Mühleberg", TM-44-80-06, Eidgenössisches Institut für Reaktorforschung, May 1980.
- [148] D. Laske, "Versuche zur Verfestigung Schwach- und mittel aktiver Abfälle mit mineralischen Bindemitteln im Hinblick auf eine Endlagerung in geologischen Formationen der Schweiz, 6 Teil: Fortsetzung vom 4. Teil, TM-44-80-1, vom 9.1.1980" TM-44-80-10, Eidgenössisches Institut für Reaktorforschung, August 1980.
- [149] D. Laske, "Versuche zur Verfestigung Schwach- und mittel aktiver Abfälle mit mineralischen Bindemitteln im Hinblick auf eine Endlagerung in geologischen Formationen der Schweiz, 7 Teil: Fortsetzung vom 5. Teil, TM-44-80-06 vom 28 May 1980", TM-44-81-01, Eidgenössisches Institut für Reaktorforschung, January 1981.
- [150] D. Laske, "Die Wasserbeständigkeit von Zementverfestigungen verschiedener radioaktiver Abfälle", TM-44-81-5, Eidgenössisches Institut für Reaktorforschung, April 1981.

- [151] A.P. Haighton, "The solidification of ion-exchange wastes Part 1 & 2", CEGB Report No. NWR/SSD/RR/70/80, July 1980.
- [152] J.H. Leonard and K.A. Gablin, "Leachability evaluation of radwaste solidified with various agents", Paper 74-WA/NE-8 presented at ASME Winter Annual Meeting, New York, November 17-22, 1974.
- [153] R.O. Lokken, "A review of radioactive waste immobilization in concrete", PNL-2654, June, 1978.