Normal and Refractory Concretes for
LMFBR Applications
Volume 2: Evaluation of Concretes for
LMFBR Applications

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EPRI PERSPECTIVE

PROJECT DESCRIPTION

Virtually without exception, conventional reinforced concrete is used for constructing nuclear power plant foundations and supports, shielding walls and floors, and containment building shells because of the eminent suitability of the material under normal design conditions. In such applications, and particularly in liquid metal fast breeder reactor (LMFBR) plants, this material is challenged by high-temperature operating environments and by the possibility of contact with sodium leaks or spills; meeting these challenges has led to complex auxiliary systems for cooling and protecting the concrete.

The recent trend in LMFBR technology toward achievement of reliability and ease of operation by utilizing inherent characteristics rather than depending on complex systems suggested another approach. That approach was to seek alternative castable construction materials which can be used at elevated temperatures and are compatible with sodium. This two-volume report for RP1704-14 and RP1704-19 is a disciplined first step in that search.

PROJECT OBJECTIVES

The basic objective of this project was to identify and characterize certain types of high-temperature or refractory concretes that may have beneficial applications in the civil engineering portions of an LMFBR plant. A few examples of such applications were offered to guide the researchers: structural service at elevated temperatures, sodium spill containment, and anhydrous shielding material (for overreactor applications). A secondary objective of the work was to report any serendipitous findings that could bear on providing a substructure which would be a heat sink rather than an energy source in the improbable event of a core melt challenging containment.

PROJECT RESULTS

The results of this project are presented in two volumes. Volume 1 consists of a selective, critical survey of material properties information relevant to the project objectives, which concern both normal portland cement concrete and various refractory concretes. This survey was based on an extensive literature search; the bibliography of consulted sources is included in this volume.

Volume 2 reports the comparison and evaluation of the high-temperature performance of various concretes and the selection of the more promising candidates for possible LMFBR applications. Based on presently available data, the report recommends that four varieties of refractory concrete be tested further since they show promise of having beneficial applications for both LMFBR and certain possible LWR applications. Specific follow-on activities are recommended in this volume.

This report should be of interest primarily to LMFBR design organizations and their sponsoring utilities or agencies. Certain aspects of this work may be of benefit in the design and operational analysis of LWR systems.

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ABSTRACT

The extensive literature on the properties and behavior at elevated temperature of portland cement concrete and various refractory concretes was reviewed to collect in concise form the physical and chemical properties of castable refractory concretes and of conventional portland cement concretes at elevated temperature. This survey, together with an extensive bibliography of source documents, is presented in Volume 1. A comparison was made of these properties, the relative advantages of the various concretes was evaluated for possible liquid metal fast breeder reactor applications, and a selection was made of several materials of interest for such applications. Volume 2 concludes with a summary of additional knowledge needed to support such uses of these materials together with recommendations on research to provide that knowledge.

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Section 1

INTRODUCTION

Concrete has important applications in nuclear reactor containments and vessels and, in particular, appears to be very effective for structures and supports in liquid metal cooled fast breeder reactors (LMFBR's). This material permits casting of massive walls that offer excellent performance in case of various destructive dynamic loads, such as hypothetical core-destructive accidents, external and internal missiles, earthquake, blasts, etc. This excellent performance is due mainly to the very large energy absorption capability of reinforced concrete, ductility of reinforcement, and absence of brittle fracture modes that are of great concern for metallic structures.

The designer, however, is unable to realize the full potential of reinforced concrete in the confinement of nuclear reactors. This limitation is due to gaps in knowledge, as well as lack of easy availability of existing knowledge with regard to thermal response of concrete. Material and structural tests indicate a significant loss of strength, stiffness, and serviceability when concrete is subjected to temperatures much greater than 100°C.

While concrete is not ordinarily considered a high-temperature construction material, practical experience has shown that concrete structures have performed adequately in service when subjected to fire or heat from industrial processes. However, some losses in strength and other mechanical properties have resulted. Under very intense or prolonged high temperature exposures, failures of concrete structures have occurred. Various methods have been developed for the design of concrete structures to withstand fire. These methods have been based on laboratory results from short duration fire tests of full-scale concrete members. Unfortunately, no comparable design methods exist for concrete exposed for prolonged periods to elevated temperatures.

Because of the lack of a design procedure and the limited knowledge of material behavior, current practice in nuclear containment design, as embodied in existing codes (Vol. 1, Ref. 21)*, avoids temperature exposure of concrete in excess of 150^oF (200^oF in special areas) under normal operating conditions.

At the same time, it is widely acknowledged that various types of high-temperature exposure of concrete would be permissible, provided one could carry out a sufficiently realistic analysis of the thermal effects, based on measurements of material properties. This is explicitly recognized by existing nuclear code requirements governing concrete temperatures, such as ASME BPV-III-2, subsection CC-3440, (Vol. 1, Ref. 21):

"(c) Higher temperatures than given in (a) and (b) above may be allowed in the concrete if tests are provided to evaluate the reduction in strength and this reduction is applied to the design allowables. Also, evidence shall be provided which verifies that the increased temperatures do not cause deterioration of the concrete either with or without load."

Any advances in this direction are likely to have a high payoff. Considerable economies would be possible in the construction of reactor structures and supports, if properly designed to operate at temperatures over 100^oC. Furthermore, the safety assessment of certain nuclear reactor systems could change considerably--for example, if a concrete structure could be relied upon to contain a spill of hot sodium from a sodium-cooled fast breeder reactor. In this sense, further advances in concrete technology could make a major contribution for economical and safe nuclear power.

Consideration cannot be limited to normal portland cement concretes. Although refractory and various other special concretes have not been used for large load-bearing structures, they offer very attractive thermal properties that might be successfully exploited. Literature on refractory concretes as well as the high-temperature behavior of normal concrete is quite extensive, but little effort

*Designates reference number given in Volume 1 of the present report.

has been made to collect and organize these data in a concise form. Two exceptions are the books by Nekrasov (Vol. 1, Ref. 232), and by Petzold and Rohrs, (Vol. 1, Ref. 253). However, these two volumes cover high temperature concrete research data published only before 1967.

Accordingly, the first task of this study was a review of existing literature on high-temperature behavior of normal and refractory concretes. This was accomplished in Volume 1 of this report. That volume serves as background for the present study. Objectives of the present report are to compare high-temperature performance of various concretes, especially refractory concretes; identify their advantages and disadvantages in various structural functions and types of exposure; and determine principal gaps in existing knowledge with the consequent needs for further research.

It must be emphasized that the purpose of this report is to select concrete materials of interest and identify those properties that make these materials potentially attractive for various LMFBR applications. It is not the purpose or intent of this report to make conclusive recommendations of materials for any LMFBR or other nuclear applications.

The final selection of materials for a nuclear reactor structure exposed to high temperature depends on many factors including design parameters, and types of accidents to be considered. Such a selection cannot be accomplished without extensive design calculations based on appropriate experimental evidence. This type of experimental and design analysis is beyond the scope of the present study.

This report identifies materials that show potential for LMFBR applications, based on available published information on high-temperature properties behavior. The report also indicates where additional data are needed before the potential of these materials for nuclear applications can be evaluated.

Among the numerous known refractory materials, this report discusses only those which show the greatest promise for LMFBR applications. Aside from normal portland cement concretes, these include: (1)

high-alumina cement concretes with different types of refractory aggregates, such as chrome ore, tabular alumina, corundum, chamotte (crushed fire brick), and refractory lightweight aggregates; (2) waterglass-bonded concretes with aggregates such as chamotte or chrome ore; (3) phosphate-bonded concretes, with aggregates such as corundum, chamotte, or refractory lightweight aggregate; and (4) magnesia concretes with chrome ore aggregate. For completeness some information will also be given on refractory brick masonry, which is not a concrete but can be substituted for it in some applications.

Although this work is motivated by the needs of a safe design of LMFBR's, its conclusions may be equally valid for important uses of materials in other reactor systems, such as light water cooled nuclear reactors.

Section 2

COMPARISON OF VARIOUS MATERIALS

To facilitate comparison of the performance of various available concretes at high-temperature exposure, a list of principal characteristic properties that the designer needs to know is presented. This information, based on Volume 1 of this report, is compiled in Tables 2.1, 2.2, and 2.3.

The listing of various properties involved in comparing materials is split into three separate tables; one on strength at various temperatures (Table 2.1), one on deformation as related to temperature (Table 2.2), and one on basic thermal properties and resistance to sodium attack (Table 2.3).

In studying these tables, it should be realized that the need for brevity prevents presentation of all qualifying conditions and range limitations. The tables are intended as a first guide. Further literature must be consulted before making a final choice.

TABLE 2.1 - STRENGTH COMPARISON TABLE

Material	Type of Test	Strength (in psi)			Remarks
		25 to 300°C	300 to 600°C	over 600°C	
(1) Normal Portland Cement Concretes with Natural Aggregates	Compressive strength, hot*	2,000 to 8,000 at 25°C to 1,700 to 6,800 at 300°C (short term)	1,400 to 5,600 at 600°C (700 to 2,800 for sili- cate aggregate concrete)	short term hot strength ~ 25% f'_c about 870°C	1. f'_c = 2,000 to 8,000 psi 2. Strength at elevated temperature increases if static load present during heating
	Compressive strength, cooled**	2,000 to 8,000 for no preheat to 1,300 to 5,200 for preheat to 300°C	0.65 f'_c after preheat to 300°C to 0.40 f'_c for preheat to 600°C (0.3 f'_c for sili- cate aggregate concrete)	Little or no residual strength after preheat above 870°C	3. Strength losses greater for long term heating 4. Use of ceramic stabil- izers reduce strength loss at elevated tem- perature
	Modulus of Rupture, hot*	Tensile and flexural strength losses comparable to compressive strength losses (losses slightly more severe)			
(2) Portland Cement + Chamotte	Compressive strength, cooled**	4,700 at 23°C to 3,800 at 300°C	3,250 at 600°C	1,400 at 1100°C	

*Hot. Properties determined while concrete was maintained at indicated temperature.

**Cooled. Concrete initially pre-heated to indicate temperature, then cooled. Properties determined at ambient temperature.

TABLE 2.1 - STRENGTH COMPARISON TABLE (Continued)

Material	Type of Test	Strength (in psi)			Remarks
		25 to 300°C	300 to 600°C	over 600°C	
(3) High Alumina Cement + Chrome Ore	Compressive strength, cooled based on Nekrasov et al	6,400 to 4,250	4,250 to 3,800	7,000 at 1200°C	
	Mitusch (20% alumina cement), cooled	4,800 to 3,550	3,550 to 2,850	2,400 at 1200°C	
	Modulus of Rupture, hot	No data	700 at 480°C	1,300 at 900°C	
(4) High Alumina Cement + Tabular Alumina	Compressive strength, cooled	7,000 to 12,000 at 110°C	7,000 to 12,000 at 538°C	7,000 to 12,000 at 816°C	High strength
	Modulus of Rupture, hot	3,000	2,100 at 480°C	1,800 at 900°C	
	If pre-fired to 1700°C	3,800	3,800 at 480°C	3,000 at 900°C	
(5) High Alumina Cement + Corundum	Compressive strength, cooled	2,650 at 300°C	2,130 at 600°C	2,800 at 1200°C	

TABLE 2.1 - STRENGTH COMPARISON TABLE (Continued)

Material	Type of Test	Strength (in psi)			Remarks
		25 to 300°C	300 to 600°C	over 600°C	
(6) High Alumina Cement + Chamotte	Compressive strength, hot (based on Nekrasov, Babcock and Wilcox)	1,000 to 1,800	1,000 to 2,100	800 to 1,100 at 1000°C	
		4,200	3,800	5,000	
	Compressive strength, cooled (based on Nekrasov, Mitusch, Rudolph, Babcock and Wilcox)	3,550 to 3,600	2,250 to 3,800	2,500 to 3,700	
		1,400 at 300°C	1,400 at 600°C	4,200 at 1400°C	
		No data	No data	2,100 to 4,000 at 1200°C	
	Modulus of Rupture, hot (based on Nekrasov, Babcock and Wilcox)	No data	1,050 at 480°C	800 at 900°C	
(7) High Alumina Cement + Refractory Lightweight Aggregates	Compressive strength, cooled density γ_3 1400 g/cm ³ density γ_3 1200 g/cm ³				For insulation
		2,000 at 25°C	1,900 at 300°C	1,400 at 600°C	
		1,400 at 25°C	840 at 300°C	560 at 600°C	

TABLE 2.1 - STRENGTH COMPARISON TABLE (Continued)

Material	Type of Test	Strength (in psi)			Remarks
		25 to 300°C	300 to 600°C	over 600°C	
(8) Waterglass-Chamotte Concrete	Compressive strength, hot If preheated to 1000°C	2,400 to 3,700	3,400 to 3,550	2,700 at 1200°C	Preheating process is good for hot and cold compressive strength, i.e., strength improves with preheat temperature
	Compressive strength, cooled	700 to 2,560	2,700 at 600°C	2,840 (at 700°C) 5,500 (at 1000°C) 6,700 (at 1200°C)	
(9) Waterglass-Chrome Ore	Compressive strength, hot	2,300 to 2,600	2,800 to 3,000	2,300 to 3,000 at 1,200°C	
	Modulus of Rupture, hot	No data	No data	800 at 650°C 1,000 at 800°C 250 at 1100°C	
(10) Phosphate-bound Corundum	Compressive strength, hot based on Babcock and Wilcox (90% Al ₂ O ₃)	2,700 to 4,800	6,700 at 600°C	8,000 at 1,200°C	1. Low initial strength 140 to 700 psi 2. Very high strength after heating up
(11) Phosphate-bound Chamotte	Compressive strength, cooled	100 at 23°C 1,200 at 300°C	1,700 at 600°C	1,600 at 1350°C	
(12) Phosphate-bound Light- weight Corundum	No data				For insulation - not structural material

TABLE 2.1 - STRENGTH COMPARISON TABLE (Continued)

Material	Type of Test	Strength (in psi)			Remarks
		25 to 300°C	300 to 600°C	over 600°C	
(13) Magnesia-bound Chrome Ore	Compressive strength, cooled	1,700 to 3,600	1,200 to 1,700	400 to 1,200 at 1200°C 3,550 to 4,000 at 1400°C	Low strength at temperature range 300°C to 1200°C
(14) Refractory Brick Dense HA Brick (Tabular alumina + high alumina cement)	Compressive strength, cooled	No data	No data	9,000 to 16,000 hard fired by manufacturer	
	Modulus of Rupture, cooled	2,500 to 3,500 hard fired	No data	No data	
Magnesia Brick	Modulus of Rupture, hot (Harbison-Walker)	1,000 to 2,000 at 230°C	No data	500 to 1,000 up to 1500°C	
	Foessel and Treffner (Phosphate-bonded)	2,300 at 300°C	1,000 at 600°C	2,600 at 1,000°C	
Zirconia Brick	Compressive strength, cooled	7,000 to 11,000 at 23°C	No data	No data	
	Modulus of Rupture	2,300 to 3,300 at 23°C	No data	No data	
Graphite Brick	No data				

TABLE 2.1 - STRENGTH COMPARISON TABLE (Continued)

Material	Type of Test	Strength (in psi)			Remarks
		25 to 300°C	300 to 600°C	over 600°C	
Dense Superduty Fireclay Brick	Compressive strength, cooled	2,000 at 23°C 4,000 at	No data	7,000 to 11,000 at 1000°C	
	Modulus of Rupture	700 to 1,500 (for normal) 2,700 to 3,700 (for prefired)	No data	No data	

TABLE 2.2 - COMPARISON OF DEFORMATION DATA

Material			Remarks
	Deformation Capacity	Thermal Expansion	
(1) Normal Portland Cement Concretes with Natural Aggregates	Ta* = 380°C 500°C (for limestone concrete)	55 to 140 x 10 ⁻⁷ /°C for normal concrete 80 to 180 x 10 ⁻⁷ /°C for limestone concrete	
(2) High Alumina Cement + Chrome Ore	Ta = 1480°C	75 to 90 x 10 ⁻⁷ /°C Chromite aggregate 60 x 10 ⁻⁷ /°C for Chrome Ore with portland cement	
(3) High Alumina Cement + Tabular Alumina	Ta = 1400°C	No data	
(4) High Alumina Cement + Corundum	Ta = 1550°C	25 to 50 x 10 ⁻⁷ /°C	High deformation capacity, low thermal coefficient of expansion
(5) High Alumina Cement + Chamotte	Ta = 1350°C	50 to 80 x 10 ⁻⁷ /°C	
(6) High Alumina Cement + Refractory Lightweight Aggregates	Ta = 1040°C (foamed alumina cement) Ta = 1100°C (smelted alumina cement)	Depend on aggregates	Poorer than the normal weight refractory concrete

*Ta = defines the temperature at which the loaded test piece is compressed by 0.6% from the point of maximum expansion.

TABLE 2.2 - COMPARISON OF DEFORMATION DATA (Continued)

Material			Remarks
	Deformation Capacity	Thermal Expansion	
(7) Waterglass-Chamotte Concrete	Ta = 1040°C Shrinkage 0.5% up to 1200°C	60 to 80 x 10 ⁻⁷ /°C	
(8) Waterglass-Chrome Ore Concrete	Ta = 1100°C	90 x 10 ⁻⁷ /°C	
(9) Phosphate-bound Corundum	Ta = 1700°C Shrinkage 0.4% up to 1500°C	60 80 x 10 ⁻⁷ /°C	
(10) Phosphate-bound Chamotte	Ta = 1300°C	60 165 x 10 ⁻⁷ /°C Alumina phosphate castable (variety depends on bonding)	With very small shrinkage at high temperature up to 1200°C
(11) Phosphate-bound Lightweight Corundum	Can be subjected to temperature up to 1500°C Ta = 1300°C	No data	
(12) Magnesia-bound Chrome Ore	Ta = 1480°C	130 x 10 ⁻⁷ /°C	
(13) Refractory Brick	No data	from 5 x 10 ⁻⁷ /°C for zirconia brick to 15 x 10 ⁻⁷ /°C for magnesia brick	

TABLE 2.3 - COMPARISON OF INSULATION AND SODIUM RESISTANCE

Material	Thermal Properties		Sodium Resistance	Remarks
	Thermal Conductivity cal/cm-sec-°C	Specific Heat cal/g-°C		
(1) Normal Portland Cement Concretes with Natural Aggregates	Normal weight 0.003 0.006 at 25°C 0.003 at 1000°C Lightweight concrete 0.001 Basalt concrete 0.0046 0.0017	0.18 to 0.28 25°C to 1000°C Basalt concrete Cp = 0.22 0.40	Not good	Use of surface treatments can increase the sodium resistance
(2) High Alumina Cement + Chrome Ore	Portland + Chrome Ore (unfired) 0.0015 0.0021 Alumina + Chrome Ore 0.0028	0.22	High Cr ₂ O ₃ , SiO ₂ and FeO content ² may react with sodium	
(3) High Alumina Cement + Tabular Alumina	0.12 to 0.17 (unfired)	0.08 0.10	Good	High conductivity due to high density, 170 pcf
(4) High Alumina Cement + Corundum	0.0055 at 25°C 0.005 at 1000°C	0.31	Good	High Cp
(5) High Alumina Cement + Chamotte	0.002	0.20 to 0.25	High SiO ₂ content may react with sodium	

TABLE 2.3 - COMPARISON OF INSULATION AND SODIUM RESISTANCE (Continued)

Material	Thermal Properties		Sodium Resistance	Remarks
	Thermal Conductivity cal/cm-sec-°C	Specific Heat cal/g-°C		
(6) High Alumina Cement + Refractory Lightweight Aggregates	Insulating chamotte 0.001 0.0005 Insulating alumina cement concrete 0.0003 0.0004 for density 0.2 g/cm ³ 0.0016 for density 1.6 g/cm ³	No data	1. Depends on aggregate chemistry 2. High porosity easily lead to chemical attack	
(7) Waterglass-Chamotte Concrete	No data	No data	High SiO ₂ content may react with sodium	
(8) Waterglass-Chrome Ore Concrete	0.0034	No data	Cr ₂ O ₃ and FeO content may react with sodium	
(9) Phosphate-bound Corundum	No data	No data	No data, but widely used in special plant to resist chemical attack	Porosity is high generally will not resist Na penetration, but no data on possible chemical interaction
(10) Phosphate-bound Chamotte	No data	No data	No data, but widely used in special plant to resist chemical attack	Porosity is high generally will not resist Na penetration, but no data on possible chemical interaction

TABLE 2.3 - COMPARISON OF INSULATION AND SODIUM RESISTANCE (Continued)

Material	Thermal Properties		Sodium Resistance	Remarks
	Thermal Conductivity cal/cm-sec-°C	Specific Heat cal/g-°C		
(10) Phosphate-bound Lightweight Corundum	No data	No data	No data, but widely used in special plant to resist chemical attack	Porosity is high generally will not resist Na penetration, but no data on possible chemical interaction
(12) Magnesia-bound Chrome Ore	0.004	No data	Cr ₂ O ₃ and FeO may react with sodium	
(13) Refractory Brick	Fireclay brick 0.0033 to 0.0052 50 °C to 1500 °C High alumina brick 0.0027 0.004 50 °C to 1500 °C	No data	Excellent: High density high alumina brick Good: Zirconia brick Questionable: Carbon brick (graphite) Superduty fire- clay brick	

Section 3

ADVANTAGES, DISADVANTAGES, AND SELECTION OF MATERIALS OF INTEREST

Now that the essential properties relevant to a comparison of various materials available have been listed, the principal advantages and disadvantages of which the designer must be aware in making a selection of materials for high-temperature exposure may be identified. Again, it should be realized that statements of advantages and disadvantages are simplified and do not permit distinguishing small differences in performance, ranges of temperature, and other parameters.

3.1 LISTING OF ADVANTAGES AND DISADVANTAGES OF VARIOUS MATERIALS OF INTEREST

(1) Normal Portland Cement Concretes with Natural Aggregates

Advantages

- (a) No preheating or prefiring is needed to develop adequate strength; needs only moist curing conditions to produce maximum strength.
- (b) Conventional concrete has a relatively high compressive strength at ambient temperatures.
- (c) The material retains a significant portion of its compressive strength on heating up to 450°F. This is true even for prolonged heating periods. For basalt aggregate concretes, the residual strength after heating more than 2 years at 450°F is about 65% of that for unheated concrete. The same behavior is true of the tensile strength. The elastic modulus loss is somewhat greater.
- (d) The material has a proven stability of microstructure and of dimensions at ambient and moderate elevated temperatures. This information is obtained from performance of gas-cooled nuclear reactor vessels and waste storage tanks.
- (e) Thermal properties up to about 500 to 700°C are acceptable if the aggregate is properly selected. Preferable is

basalt or limestone, but even siliceous aggregate concretes perform relatively well below 540°C.

- (f) The material has relatively low conductivity, making it a good (but not superior) insulating material.
- (g) Relatively extensive information on thermal properties and performance is already available in the literature. However, certain conspicuous gaps exist, particularly for the case of prolonged heat exposure.
- (h) Design and construction technology are well developed, although for the case of high temperature applications they may be much too conservative.

Disadvantages

- (a) The material liberates much water on heating, particularly at temperatures over 500°C.
- (b) Creep increases significantly as a result of heating and is much larger than for certain other refractory materials. Related to this is a significant drop of the apparent short-time elastic modulus.
- (c) At temperatures under 500°C the loss of strength is relatively minor. However, it becomes significant at higher temperatures. At 760°C the strength is near zero.
- (d) The loss of water as well as significant thermal deformation and thermal shrinkage may lead to significant cracking at temperatures above 100°C, depending on the particular design and reinforcement.
- (e) Material is susceptible to explosive spalling from rapid heating in moist condition, particularly under conditions of restraint. However, counter-measures in design seem possible.
- (f) If unprotected, the material is quite susceptible to sodium attack. The performance depends on many conditions including surface exposure conditions, reaction product transport, surface sodium convection, reinforcement, restraint, and dimensions.

(2) High-Alumina Cement (HAC) Concretes

Advantages

- (a) Like portland cement concretes, these concretes harden and gain strength at ambient temperature. No heat-treatment is required to develop strength.

- (b) Compressive as well as tensile strength of this material is relatively good and comparable to that of portland cement concrete.
- (c) If pre-fired above 1000°C , this material retains significant strength at much higher temperatures than portland cement concretes. This is due to the formation of ceramic bonds at firing temperatures above 1000°C .
- (d) After firing, thermal deformations are reversible and easily predictable. That is, after firing, no further permanent length changes occur with subsequent heating and cooling.
- (e) After firing, aluminous cement concretes using high-quality refractory aggregates, such as chamotte and chrome ore exhibit smaller creep deformations at elevated temperatures than portland cement concretes.

Disadvantages

- (a) To obtain maximum strength at temperatures above 600°C where portland cement concrete cannot serve, and to achieve reversibility of deformations, the material must be fired at temperatures over 1000°C . While this is no problem for small blocks or thin linings used in chemical processing technology vessels, the need for firing presents formidable difficulties when massive nuclear reactor structures are considered.
- (b) High alumina cement concretes are susceptible to the well-known conversion reaction (Vol. 1, Ref. 247). This can lead to loss of strength at temperatures slightly above ambient. The probability of conversion occurring can be reduced by controlling temperatures during curing. Conversion reactions occur when hydrated aluminous cement concrete is heated. These reactions lead to some loss of concrete strength. However, with care in mix design and curing, residual strengths may be adequate for structural applications at elevated temperatures. Firing concrete at 1000°C can eliminate the conversion problem, since fired concrete has high strength due to permanent ceramic bonds, not to formation of hydration products.

- (c) Without firing, these refractory materials are not as chemically stable as portland cement concretes at lower temperatures.
- (d) High-alumina cements develop considerably higher hydration heat than do portland cements. This causes large thermal expansions, particularly in more massive concrete walls in which the hydration heat produces a large temperature rise. This presents difficulties in the design of these structures against cracking. However, even in a massive structure the deleterious effects of hydration heat can be eliminated by cooling through pipes embedded in the concrete.
- (e) Drying shrinkage of high alumina cement concretes on heating is generally larger than for portland cement concretes. This makes the structure more susceptible to cracking, due to the higher water requirements for curing.
- (f) Compared to portland cement concretes, mechanical behavior of these materials is generally less well understood, owing to their lack of use in structural load-bearing applications. The technology of design and construction is less developed than that for portland cement concretes.
- (g) Overall, for moderately high temperatures (up to 400°C) high alumina cement concretes appear to afford no significant advantages over portland cement concretes for structural applications. Their main advantages are realized at temperatures above 600°C, where normal portland cement concrete has little or no strength.

A more detailed discussion of high alumina cement concretes with different types of aggregate follows.

(2a) High Alumina Cement Concrete with Chrome Ore Aggregate Advantages

- (a) This aggregate gives the material very good creep resistance. Creep deformations are quite low compared to normal portland cement concrete. The same is true of shrinkage. Even 15 to 20% of finely ground chrome ore added to the mix significantly reduces shrinkage.
- (b) The use of chrome ore also increases strength.

- (c) Thermal conductivity is low compared to concrete made with other normal weight aggregates. The material has good insulating properties.

Disadvantages

- (a) Chromite, the main constituent of chrome ore, is sensitive to oxidation. This leads to the formation of Fe_2O_3 from FeO and results in a destruction of refractory spinel structure. Control of the atmosphere of the firing furnace is therefore very important.
- (b) Tests on refractories incorporating chrome ore aggregates have shown strong reactivity to molten sodium, even when chrome ore is present only as a minor constituent (10 to 15% of total aggregate volume).

(2b) High Alumina Cement Concrete with Tabular Alumina Aggregate (99%+ Al_2O_3)

Advantages

- (a) If prefired at 1700°C , the material exhibits high strength (modulus of rupture) at temperatures up to 1500°C .
- (b) In the case of high purity tabular Al_2O_3 , the aggregates show excellent resistance to molten sodium attack.
- (c) Highly refractory material withstands service temperatures of 1800°C .

Disadvantages

- (a) Firing to 1700°C is difficult and expensive.
- (b) Knowledge of the mechanical properties of this material is quite limited. No data seem to exist for hot compressive strengths.
- (c) Concrete exhibits high thermal conductivity and creep at elevated temperatures, compared to other refractory concretes.
- (d) Cost of high purity tabular alumina aggregate is very high.

(2c) High Alumina Cement Concrete with Corundum Aggregate (50 to 90% Al_2O_3)

Advantages

- (a) Coefficient of thermal expansion is low ($60 \text{ to } 80 \times 10^{-7}/^{\circ}\text{C}$).
- (b) Melting point is high ($\sim 1800^{\circ}\text{C}$).
- (c) Strength is high (2800 psi in compression at 1200°C).
- (d) Chemical resistance is generally good.
- (e) Use of ground corundum tends to reduce drying shrinkage of heated concrete.
- (f) Heat capacity is high.
- (g) If Al_2O_3 is of high purity, resistance to sodium attack is good.

Disadvantages

- (a) Thermal conductivity is relatively high.
- (b) Cost of corundum aggregate is high.

(2d) High Alumina Cement Concrete with Chamotte Aggregate

Advantages

(Chamotte is the highest quality, very dense, crushed fire brick.)

- (a) Since this is the most commonly used refractory concrete, a large body of experience is available.
- (b) High compressive strength can be achieved through proper firing.
- (c) Thermal conductivity is low, making the material a good insulator.
- (d) Resistance to wear damage is good, although this is of no advantage for nuclear reactor structures.

Disadvantages

- (a) High content of SiO_2 (50 to 85%) makes the material very susceptible to reaction with molten sodium.

(2e) High Alumina Cement Concrete with Refractory Lightweight Aggregate

Lightweight refractory aggregates include vermiculite, pearlite, crushed insulating firebrick, and bubbled alumina.

Advantages

- (a) The use of lightweight aggregates produces insulating refractory concretes with thermal conductivities $1/3$ to $1/10$ that of comparable normal weight refractory concretes.

Disadvantages

- (a) The use of lightweight aggregate produces concretes with relatively low compressive strength.
- (b) Volume stability of the material is lower than for normal refractory concretes.
- (c) High porosity of the lightweight aggregate facilitates molten sodium penetration and chemical attack.

Several types of non-hydraulic binders, in particular the phosphates, magnesia, and waterglass binders will now be considered. These do not chemically combine water in order to harden, although they need water in the mix.

(3) Phosphate-Bonded Concretes

(3a) Phosphate-Bound Corundum

Advantages

- (a) Very good thermal shock resistance.
- (b) Very high operating temperature limit can be reached, about 1800°C.
- (c) Retains compressive strength at high temperatures (8000 psi at 600°C).
- (d) Apparent porosity is very low; after firing at 1600°C it is almost zero.
- (e) Shrinkage produced by firing temperature is almost negligible, being generally under 0.4%.
- (f) The material can exist in various forms, such as cold-setting concrete, sprayed concrete, and heat-setting tamped concrete.
- (g) Abrasion resistance is excellent (40 times higher than normal fire brick).
- (h) The material is particularly suited for repair patches particularly in furnace liners or coal gasification reactors.
- (i) Resistance to various forms of chemical attack is generally excellent (in particular, high resistance to chloric gases at high temperatures).

Disadvantages

- (a) The initial compressive strength is low when air-dried (140 to 700 psi at ambient temperature).

These materials must be preheated to 350°C to develop adequate mechanical strength.

- (b) Strength achieved is quite sensitive to the heating process and mix proportions.
- (c) Gaseous expansion can sometimes occur during the drying or heat treating process (this is attributed to the development of hydrogen formed by a reaction between the residues of metals and acids, and can be counteracted by adding inhibitors).
- (d) The hot tensile strength (modulus of rupture) drops appreciably at temperatures over 1000°C.
- (e) The volume stability at temperatures over 1200°C is poor.

(3b) Phosphate-Bound Chamotte

Advantages

- (a) This material has a particularly low drying shrinkage on heating.

Disadvantages

- (a) The initial strength is very low, unless heated to 350°C.
- (b) Gaseous expansion is possible.
- (c) The high content of SiO₂ in chamotte aggregate is likely to promote molten sodium attack.

(3c) Phosphate-Bound Lightweight Corundum

Advantages

- (a) This is a very good insulating material, as are all lightweight aggregate concretes.

Disadvantages

- (a) The compressive strength is generally low, even after heating or firing.
- (b) The high porosity makes the material susceptible to chemical attack by molten sodium.

(4) Magnesia-Bound Chrome Ore Concrete

Advantages

- (a) This material has a very good compressive strength at temperatures over 1400°C.

Disadvantages

- (a) Requires firing to temperatures of 1200°C to develop usable strength for structural applications.

- (b) Initial strength is very low.
- (c) Heat conductivity and thermal expansion are relatively high.
- (d) The high content of Cr_2O_3 may be expected to promote molten sodium attack.
- (e) Creep and shrinkage are generally higher.

(5) Waterglass Concretes

The term "waterglass" denotes an aqueous solution or colloidal dispersion of various hydrolized sodium or potassium silicates. The composition and ratio of SiO_2 to Na_2O may vary in practice.

Advantages

- (a) Waterglass is a non-hydraulic binding agent. It does not chemically combine water as it hardens. However, water must be present in the mix.
- (b) The material hardens and gains strength at relatively low temperatures (100°C), at which point it loses the mix water, provided that the layer is sufficiently thin to allow migration of the water to the outside. The absence of water in dried concrete ought to be advantageous in case of sodium attack. Also, waterglass undergoes beneficial bonding reactions with a wide variety of refractory aggregates that lead to retention of strength at temperatures greater than 1000°C .
- (c) Experience with waterglass-bonded concretes in refractory applications indicates that these materials are resistant to sodium vapor and its oxides.

Disadvantages

- (a) Waterglass concretes have no appreciable strengths unless heated to above 100°C . The compressive strength of heated/dried concrete is not very high when compared to other concrete systems discussed in this report.
- (b) Escape of water during heating leaves a significant pore space. This suggests heated concrete may be too permeable for sodium containment applications. However, Petzold and Rohrs cite one study where waterglass concretes were produced with low permeability in both unfired and fired states. (Vol. 1, Ref. 253, p. 174).

- (c) The large porosity and low strength make the performance of the material under sodium attack quite suspect in spite of the probable unreactivity of sodium silicate with sodium. However, hard data are lacking.

(5a) Waterglass - Chamotte Concrete

Advantages

- (a) In addition to general advantages listed previously, waterglass-chamotte undergoes relatively small drying shrinkage on heating (approximately 0.5%).

Disadvantages

- (a) High silica content of chamotte aggregate is susceptible to attack by sodium.

(5b) Waterglass - Chrome Ore Concrete

Advantages

- (a) Deformation capacity of this concrete is greater than that of other waterglass-bound refractory concretes.

Disadvantages

- (a) Chrome ore aggregate is susceptible to attack by sodium. Because of their high porosity ranging from 20 to 25% if unfired, waterglass concretes as well as other refractory concretes do not seem to be ideal for the containment of molten sodium. However, in view of the chemical nature of waterglass, (sodium silicate) it is probable that this binder would be unreactive with molten sodium and its oxides. It seems likely that sodium-resistant waterglass-bound concretes are feasible if sodium-resistant aggregates such as corundum, tabular alumina, and periclase are used. However, no data on waterglass concretes using these resistant aggregates were found in the literature. Additional work on the sodium resistance of waterglass-bound concretes is desirable.

(6) Refractory Brick Linings (Masonry)

Although not a concrete, these materials may serve similar functions.

Advantages

- (a) The compressive strength of the lining is almost as high as the compressive strength of the bricks.

- (b) Refractory bricks can withstand very high temperatures, depending on type of brick. For example, crushing strength of superduty fireclay brick at 1260°C is essentially the same as at room temperature.
- (c) The only significant porosity occurs at joints between the bricks. If the width of joints is kept very small, overall porosity of the lining is also small.
- (d) If joints are thin, overall thermal expansion coefficient of the lining is close to that of the bricks.
- (e) Shrinkage of bricks on heating is negligible since they are prefired during manufacture.
- (f) Refractory bricks are in many cases highly resistant to sodium. They are used as linings in sodium production vessels.
- (g) Since bricks are fired to over 1000°C during manufacture, they contain no water. No hydrogen is generated by contact with sodium.

Disadvantages

- (a) The tensile strength of brick linings is generally very low.
- (b) Joints between bricks constitute a weak part of the system from the load-carrying ability view-point. As an alternative, dry joints could be contemplated for extremely well fitting bricks or blocks, but dry joints would still represent an open pore space.
- (c) If a wet mortar is used in the joints, then water will be released from the joints upon heating. If preheated, the escape of water creates pore space in the joints. Although the bricks may be resistant to the sodium, the pore space in joints caused by loss of water from the binding agent used to mortar the joints can make the lining susceptible to sodium attack.

The fact that bricks can be manufactured to essentially zero open porosity seems favorable with regard to the penetration of molten sodium. The chemical resistance to sodium attack is more difficult to assess. Sodium resistance of bricks that contain large quantities of silica (such as fireclay brick) or chrome ore may be questionable. A recent study showed that materials containing silica or chromite

are not completely chemically stable in the presence of molten sodium (Vol. 1, Ref. 10).

One report from a refractories manufacturer indicates that a dense fireclay brick had been used successfully for years as a liner in a vessel for producing sodium electrolytically at temperatures up to 1200°F from molten sodium chloride (Vol. 1, Ref. 57). On this basis, it appears that heavy duty hard-burned fireclay brick should satisfactorily resist a sodium spill of limited duration.

Based on results of the SRI study (Vol. 1, Ref. 10) as well as studies by Fink et al (Vol. 1, Ref. 112, 113) the following refractory bricks seem to be best for sodium containment: dense high alumina brick (porosity under 2%), magnesia brick (porosity about 10%), and zirconia brick (porosity 28%). These bricks showed no evident deterioration on heating in molten sodium at 850°C for five hours.

Other bricks, which have shown mixed results, some bricks being attacked others not, included: vitreous carbon or graphite brick (porosity under 1%), and dense superduty fireclay brick (porosity under 4%).

3.2 IMPROVEMENT OF PERFORMANCE

As already discussed, some of the disadvantages of castable materials may be mitigated by special measures, which are described in the following section.

Refractory Aggregates for Portland Cement Concrete

One area that deserves deeper study with regard to nuclear applications, is the improvement of heat-resistant properties of portland cement concretes. This can be accomplished by the use of refractory aggregates and finely ground ceramic fillers, such as crushed hard-burnt fire brick, chamotte, use of blast furnace slag and slag portland cements, and refractory lightweight aggregates.

Various successful applications of portland cement concretes with such refractory aggregates have been reported (Vol. 1, Ref. 253) up

to temperatures of 1100°C, however, the properties of such concretes such as strength at high temperature, elastic modulus and creep are not well characterized. It is not at all clear whether successful applications can be made in load-bearing structures for nuclear reactors. If all the important mechanical properties at high temperature were sufficiently researched, these might be attractive materials.

Fiber Reinforcement

For various applications of refractory concretes in chemical processing technology (Vol. 1, Ref. 251), stainless steel fibers added to the concrete mix can substantially improve its performance in tension. The fibers inhibit the formation of distinct continuous cracks and cause the cracking to consist of finely distributed micro-cracks that are generally discontinuous. Although the addition of steel fibers has hardly any effect on tensile strength limit, it endows the material, even without reinforcing bars, with a considerable ductility and energy absorption capability. Fracture toughness is appreciably improved. In consequence of this, the resistance to thermal shock is also improved. Addition of steel fibers also improves compressive strength by holding the material together laterally.

As indicated in the preceding volume of this report, the efficiency of steel fibers is much less documented for high temperature applications than it is for structures at normal temperature. Nevertheless, it is reasonable to expect that the addition of steel fibers would lower the chances of the formation of a catastrophic leak through a concrete containment wall. In case of a sodium spill, the action of the steel fibers should be to hold the fractured pieces of the material together, reduce the formation of continuous cracks, and significantly decrease the rate of penetration of sodium and heat into the concrete by decreasing the surface area that can be accessed by the sodium.

Similarly to conventional steel bar reinforcement, steel fibers may become ineffective at temperatures over 900°C where the creep of steel becomes very large. For such situations, exploration of the use of ceramic fibers such as glass or boron fibers or certain mineral fibers may be of interest. However, these fibers are

generally less efficient at moderate temperatures due to their lack of ductility.

Reinforcement and Anchors

Steel reinforcement and anchors may be one very effective means of improving the resistance of a refractory concrete wall to heat shock or sodium spill. This is however generally considered as a design measure rather than a material property.

Surface Treatment

The disadvantages of reactivity of concrete with sodium can be mitigated by certain surface treatments (see Vol. 1). These include impregnation of the surface with a refractory compound that is inert to sodium, such as MgO , Al_2O_3 , or sodium silicate (waterglass). This treatment reduces the internal surface area over which the compounds reactive with sodium (siliceous compounds) can come in contact with sodium, and reduces surface porosity, thereby limiting physical penetration of sodium into the concrete. However, no data on the effectiveness of these treatments for improving sodium resistance seem to exist at present. Therefore, the effectiveness of such surface treatment for resistance to sodium attack should be investigated.

3.3 RANKING OF MATERIALS FOR VARIOUS PROPERTIES

So far various castable materials have been considered and their advantages and disadvantages for potential use in LMFBR's have been listed. It may be helpful to supplement this by ranking of these materials for different properties. It must be understood, however, that this ranking is crude since some properties are not always strictly comparable. This is due to the lack of data for all materials over the complete range of time, temperature, and environmental conditions of interest.

(1) Strength

(a) Cold Compressive Strength*

Excellent

- Bricks - including hard-burned fireclay brick (7-11 ksi compressive strength), fired zirconia brick (about the same strength), and hard-burned high alumina brick** (9-16 ksi strength);
- Concretes - high alumina cement concretes (assuming no conversion reaction) and phosphate-bound corundum (which can reach 8,000 to 22,000 psi strength after proper preheat).

Good

- Bricks - hard-burned magnesia brick;
- Concretes - portland cement concretes (2 to 8 ksi compressive strength), waterglass concretes (2 to 3 ksi if preheated), and magnesia-bound chrome ore concrete (3 to 4 ksi if preheated above 1200°C).

Poor

- Lightweight insulating bricks;
- Lightweight insulating concrete;
- Magnesia-bound concrete, if preheated below 1200°C.

Uncertain

- There exists little or no data on the strength and other mechanical properties at ambient or elevated temperatures of non-hydraulic binder concretes (waterglass, phosphates, magnesia);
- Graphite brick.

(b) Hot Compressive Strength (up to 900°F)

Excellent

- Probably most bricks listed as excellent in the preceding item, but little data exist.

*Cold compressive strength. Strength of materials at room temperature. Materials previously preheated to develop ceramic bonds where indicated.

**High-alumina brick consists of tabular alumina in a high alumina cement matrix.

Good

- Portland cement concretes and high alumina cement concretes (of which the latter show a greater strength loss).

Uncertain

- Phosphate, waterglass, and magnesia-bound systems at temperatures under 1000°C.

Information on the strength after long-term heating is unavailable for all these materials, except for some data for portland cement concretes.

(c) Tensile Cracking and Fracture

Excellent

Although concrete, cold or hot, has low tensile strength and fracture toughness, reinforcement can endow the material with excellent overall tensile strength that allows distributed tensile cracks to form. Steel reinforcement, even when made of some heat-resistant steel, cannot serve effectively above 900°C (due to very large creep). The same is true of steel fibers. At temperatures of over 900°C most concretes become ductile and tensile creep is a greater problem than tensile cracking.

Good

Fired refractory concrete and brick have a good tensile strength, but this is of little use since the joints between blocks or bricks do not.

Poor

All brick systems as well as prefired concretes have a poor resistance to tensile cracking. The goal is not to eliminate tensile cracking but to live with it and exploit it, through the use of proper reinforcement, for other advantages, especially energy absorption capability.

Possible Improvement

Addition of steel fibers reduces crack propagation. This makes the material more ductile.

(2) Thermal Deformation and Volume Stability
at Elevated Temperature

Excellent

- Hard-burned zirconia or silicon carbide brick;
- Hard-burnt fireclay brick (above 1000°F);
- High alumina cement concretes of all types (if without MgO); especially those with corundum aggregates;
- Phosphate-bound corundum concretes.

Good

- High alumina brick;
- Most phosphate-bonded concretes;
- Most waterglass-bonded concretes.

Poor or Uncertain

- Portland cement concretes, particularly at temperatures over 500°C;
- Magnesia-bound concretes (high thermal expansion, unknown creep);
- Hard-burned fire-clay brick (below 1000°F);
- Magnesia brick (high thermal expansion and unknown creep).

(3) Thermal Insulation

Excellent

- Most lightweight aggregates concretes and lightweight bricks, which generally have thermal conductivities 1/3 to 1/10 that of normal weight materials.

Good

- Concretes with non-hydraulic binders (phosphate, waterglass, and magnesia);
- Portland cement concrete;
- High alumina cement concrete.
(all with no silica or magnesia)

Fair or Poor

- All high density bricks: superduty fireclay bricks, high density alumina brick, magnesia brick, etc.;
- High alumina cement concretes with tabular alumina aggregate;
- All concretes with significant amounts of silica or magnesia in the aggregate; also those with silicon carbide.
(Note that higher density works against thermal insulation capabilities.)

(4) Resistance to Sodium

Excellent (no penetration, no reaction)

- Dense hard-burned high alumina brick;
- Zirconia brick (however, one case of cracking was reported);
- Magnesia brick.

Good (either no penetration or no reaction)

- High alumina cement concrete with corundum aggregate (no reaction;
- Waterglass-bonded tabular alumina, corundum, or magnesia aggregates (possibly-no data).

Questionable

- Generally concretes of all types, because of their significant porosity;
- Fireclay brick, because of its high content of SiO_2 , which reacts with sodium;
- Chrome ore brick as well as concrete, they both react with sodium;
- Portland cement concretes, although it seems that deleterious effects may be reduced by proper designs which do not allow deep penetration of the sodium.

Possible Improvement

Improvement of performance could be achieved by surface treatment. Impregnation of pores near surfaces with a compound inert to sodium, such as MgO or Al_2O_3 , and addition of glass fibers that tend to inhibit formation of cracks through which the sodium can penetrate into the concrete may be helpful.

(5) Creep and Decrease of Stiffness

Excellent

All fired refractory bricks and most fired refractory concretes. This is due to the strong, brittle nature of ceramic bonding. Creep of fired refractories is generally less than that of portland cement concrete at elevated temperatures (up to 600°C). Above 600°C creep deformations of refractories increase. Chrome ore concretes show better resistance to creep deformations than refractories made with other aggregates.

Relatively little data are available on modulus of elasticity of refractory concretes or masonry.

Fair or Poor

- Portland cement and unfired refractory concretes (both hydraulic and non-hydraulic binders) that exhibit an order of magnitude increase in creep upon heating.

(6) Workability--Possibility to Cast Massive Containment Wall Structures

Excellent

- Portland cement concretes. Technology well developed. No special heat-treatment or curing required.

Fair or Poor

- High alumina cement concretes and practically all other refractory concretes and brick linings. Their casting in large volumes is limited by hydration heat, by the need of firing at very high temperatures, or by the need for joints between bricks.

3.4 SELECTION OF MATERIALS OF MAIN INTEREST

As can be seen from the preceding discussions, there exist many materials of interest for further study with regard to nuclear structures. None of these materials, however, are proven ready for use.

For some, such as the portland cement concretes, a large body of knowledge already exists and relatively small amount of work is needed to evaluate the applicability of these materials for nuclear structures exposed to high temperatures. For others, although existing data are promising, a large amount of additional research would have to be conducted. The use of these materials should obviously be considered as a longer range goal. Besides, not all of these materials and all of their properties would fit within the scope of a reasonably sized research program. Therefore, selection of only a few of the most promising materials for immediate study and design considerations is in order.

Thus, although the risk of uncertainty due to incomplete information exists, it seems desirable to identify several materials of greatest interest. Based on information available, these materials are as follows:

(1) Portland Cement Concretes

Portland cement concretes appear to be the best candidate for structural applications for service temperatures in the range from ambient to 300 or 400°C, provided many temperature cycles of large magnitude are excluded. Only heat resistant, carefully selected aggregates, such as basalt, limestone, or serpentine, should be used for these concretes. For an accident type exposure, such as a sodium spill, temperatures up to approximately 600°C may well be acceptable for limited periods of time if a limited damage to the structure is permitted. It is imperative that the structure is properly designed to guarantee that the damage would indeed be limited such that no leak outside the containment would occur.

For the use of portland cement concretes, various technological improvements should be considered. One idea, which has been developed to some extent at Argonne National Laboratory (Vol. 1, Ref. 31), is the hot-dried portland cement concrete vessel that is deprived by moderate heating of all evaporable water. No high temperature heating that would drive out any of the chemically bound water is contemplated since it would reduce the strength. This treatment, which increases the strength of concrete if carried out without cracking the concrete, diminishes the creep and reduces the amount of water that can react with sodium in case of a sodium spill.

Any use of portland cement concretes above a temperature of 150°F, the maximum temperature permitted by current nuclear reactor containment and pressure vessel codes, requires special design procedures and additional research. This will be further discussed in the next section.

(2) High Alumina Cement (HAC) Concretes

Portland cement concretes can be considered for sustained temperatures over 300 or 400°C and for short time exposures over 600°C. For more severe temperature conditions alternatives to normal portland cement concretes must be considered. High alumina concretes represent one alternative material for which relatively extensive information and experience already exists. It is doubtful, however,

whether anything would be gained by the use of these materials if they are not prefired.

Although HAC concretes have higher moist-cured strengths than portland cement concretes, this advantage is lost at temperatures above 50°C due to deleterious effects of conversion reactions of the hydrated HAC paste. For this reason, the use of HAC is not permitted in the U.S. for normal structural applications. However, residual strengths of HAC concrete after conversion may still be sufficient for structural applications at elevated temperatures.

If prefired to 1000°C, these materials may be able to serve structural functions at temperatures greater than 600°C. However, the need for firing presents a major technological difficulty. It would probably be extremely cumbersome and difficult to fire large monolithic structures of high alumina concrete. A more likely form of use are small blocks or panels that can be fired in a normal size furnace.

A problem then arises with regard to joints between the blocks. Either the joints use some sort of mortar, as thin a layer as possible, or they are left dry. The use of mortar in the joints implies that some water will always be contained in the mortar and will be evaporated upon heating, thus being available to react with sodium in case of a sodium spill. If the joint is dry, questions arise with regard to the strength of the structure as a whole particularly for shear loading. However, appropriate design measures, such as the use of shear keys and prestressing, could be used to provide for transfer of shear loads. Another question connected with dry joints is the possibility of access for the molten sodium into the joints. The potential for penetration of sodium into structural joints could be determined experimentally by small-scale testing.

As for the mortar to be used in joints between bricks, the use of either high alumina cement mortar or waterglass mortar seems preferable. The former hardens at room temperature, while the latter requires only moderately high temperatures of 100 to 200°C to harden. In addition, both seem to be acceptable in case of sodium spill.

(3) Non-hydraulic Concretes

For temperatures up to about 1000°C , non-hydraulic concretes such as waterglass concrete and phosphate or magnesia concretes, do not seem to offer any particular advantages over aluminous cement concretes except for the relative ease that water can be removed from these systems. They are often favored in chemical processing technology methods because of their easy casting and chemical resistance. However, the fact that they have essentially no strength unless they are heated is inconvenient, particularly in casting more massive structures. They do not have to be heated as high as alumina concretes to form a permanent high-temperature resistant bond. However, ambient temperature strengths achieved with non-hydraulic cement concretes pre-heated to temperatures of about 200°C are relatively low compared to other refractory concretes. They are less than that of high alumina cement achieved without any pre-heating, or pre-heating to 200°C . However, the strength of HAC concrete as a function of temperature is difficult to assess, owing to the variable effects of "conversion" of HAC strength. For this reason, strict comparison of these concretes is not always possible.

The high porosity of these materials casts doubt on their performance in case of sodium attack, because a much higher internal surface can be exposed to sodium. This may be a problem even if their chemical activity is very small. However, these are only opinions based on the present limited knowledge, and further investigations are in order.

One use of non-hydraulic concretes is for the case of temperatures in excess of 1000°C . Non-hydraulic concretes can serve structural functions by maintaining adequate strength and limited deformation at temperatures up to 1800°C . These conditions are required for containing a steel melt without any significant damage to the wall. A very thick portland cement concrete wall can also contain a steel melt, but only if the melt cools before disintegration of concrete can progress through the wall.

(4) Refractory Brick Systems

Concrete or refractory concrete lined with a layer of refractory brick, with or without a steel liner, is obviously of interest for very high temperatures, as an alternative to non-hydraulic concretes. A sufficiently thick lining of refractory bricks is able to contain a steel melt. Certain special bricks, such as zirconium oxide or carbide can contain melts at temperatures over 2000°C, such as in the case of molten uranium oxide.

In contrast to all concrete systems, dense refractory bricks have the advantage of very low apparent porosity, almost zero for certain bricks. This makes them highly attractive for containing a sodium spill.

Refractory bricks are usually pre-fired by the manufacturer. Thus, no additional heat-treatment is required when bricks are installed. Dense refractory bricks usually have very high cold crushing strengths, up to 16,000 psi, and retain considerable strength on heating.

Resistance of refractory brick to chemical attack from molten sodium is more difficult to assess than the problem of physical penetration of sodium, although the two phenomena are inter-related. Two experimental studies (Vol. 1, Ref. 9, 112, 113) have indicated that the following brick types show promise for molten sodium containment:

High density high alumina brick	(open porosity 2%)
High density magnesia brick	(10%)
Zirconia brick	(30%)

Two other brick systems have shown some limited capacity for resisting chemical attack of molten sodium:

Vitreous carbon or graphite brick	(open porosity 1%)
Dense superduty fireclay brick	(4%)

Fireclay brick has reportedly been successfully used to line vessels used for producing sodium electrolytically from molten sodium chloride (Vol. 1, Ref. 57). However, laboratory tests of fireclay brick

exposed to molten sodium at 870°C have resulted in complete destruction of the brick.

Since bricks are pre-fired during manufacture, all water is removed, and no additional heat-treatment is required. The use of mortar to bind bricks will introduce some water into the masonry system, but amount of moisture present will be much smaller than that present in a concrete liner. Alternatively, the use of dry-joint masonry construction methods would eliminate the need for mortar.

3.5 MATERIALS OF INTEREST FOR TYPICAL APPLICATIONS IN LMFBR

Having described individual materials and properties of interest, this information will now be related to particular applications in LMFBR's. These are as follows:

A. Structural (Load-Bearing) Service at Temperatures Up to 400°C

Within this temperature range the use of portland cement concretes seems to be preferable. Complete design procedures for temperatures over 150°F (present code limit) however, are not available at present and further work needs to be done. No refractory concrete or brick system seems to offer any definite advantages over portland cement concrete in this temperature range. Portland cement concrete can be produced to have within this temperature range adequate strength, by compensating for losses due to heating, as well as limited deformation.

Certain design measures may also be considered to improve the performance of portland cement concrete in this temperature range. These include drying of the concrete by sustained mild heating that drives out the evaporable water but not the chemically-bound hydration water. The thermal expansion, thermal shrinkage, creep, resistance to cracking, and bond with steel, appear to be all acceptable within this range and not very different from these properties at room temperature. The open question is the proper design procedure, that is the need to calculate stresses, predict cracking and fracture behavior as well as creep and shrinkage deformations, with sufficient accuracy to assure the desired performance.

B. Liquid Sodium Containment Up to 880°C

Even for this application, portland cement concretes may prove to be acceptable. A wall made of portland cement concrete may undergo a considerable amount of damage when exposed to a sodium spill. A large part of the thickness of the wall may be destroyed, and the consequent development of hydrogen gas in the containment must be handled. However, the ultimate goal of containment may still be achieved with appropriate design measures. These include a layout of reinforcement that inhibits cracking of the wall, spalling of its fragments and provides sufficient restraint (compressive confining stresses). The use of steel fibers to distribute cracking and minimize formation of fragments may also be helpful.

Regarding sodium containment other materials are preferable to portland cement concretes. High alumina cement concretes would probably perform better if only because they do not contain large amounts of silica. The best performance would be provided by dense refractory brick linings, owing to their low porosity as compared to concretes. This is confirmed by the fact that such a lining is used in vessels for production of sodium, and verified in laboratory tests of various refractory brick systems exposed to molten sodium. Such a lining can be designed to suffer no damage in exposure to sodium. The designer must weigh the cost and other complexities of doing this against the consequences or acceptability of a severe but limited damage to a portland cement concrete structure.

Waterglass concrete is questionable in this application because of its high porosity and presumed high permeability and low strength, even though the chemical reactivity of waterglass with liquid sodium may be negligible. Further information is needed on permeability of waterglass concretes to molten sodium.

For concrete exposed to liquid sodium, the choice of aggregate is extremely important. As a general rule, aggregates containing silica or chrome ore should be avoided where resistance to sodium is required. The aggregates of best performance are as follows: refractory aggregates - tabular alumina, corundum, zirconia, silicon carbide, and magnesia; normal aggregates - basalt, limestone.

C. Radiation Shielding at Temperatures from Ambient to 650°C

Inasmuch as neutron radiation shielding depends on the content of hydrogen molecules, it should be recognized that portland cement concretes as well as unfired high alumina concretes always contain a large amount of hydrogen. Even when their evaporable water is driven out due to heating, there still remains in the material a large amount of chemically-bound water. The wall thickness required for structural reasons is usually adequate to provide adequate shielding with appropriate choice of aggregates.

The radiation shielding characteristics of concrete have been discussed extensively elsewhere in the literature. Biological shielding of neutrons and gamma rays has been achieved by incorporating aggregates that efficiently attenuate these types of radiation. Since neutrons are heavily attenuated by hydrogen, usually in the form of water, or boron atoms, aggregates containing either element have been used. These include: serpentine, bauxite, limonite, boron carbide, or boron frit. Serpentine and bauxite will retain their chemically-bound water when heated to temperatures above 100°C, but will lose all water when heated to 1000°C. Boron melts at around 2000°C, while boron carbide has a melting point of about 2450°C. With such high melting points, boron and its carbide can be considered "refractory", however, no data were found on their use in refractory concretes. By contrast, aggregates commonly used in refractory concretes do not show any pronounced capability for shielding neutron radiation.*

Gamma radiation is effectively attenuated by incorporating aggregates of high density in concrete used for biological shielding. These include: magnetite, hematite, barite, or even steel punchings. A number of dense refractory aggregates used in concrete or bricks have high specific gravities which may make them suitable for gamma radiation shielding. Among these are: zirconia (6.5)**, chrome ore

*Bonilla, C.F., Nuclear Engineering, McGraw-Hill, 1957, pp.863-841.

**Numbers in parentheses are mineral's specific gravity. For comparison, Sp. Gr. of water = 1. Sp. Gr. normal concrete = 2.3 to 2.4. Sp. Gr. steel = 7.6 to 8.0.

(4.5), corundum and tabular alumina (4.0), magnesia (3.6), and silicon carbide (3.2).

Normal weight refractory concretes incorporating these aggregates have bulk specific gravities lower than that of the aggregate, due to the high porosity (approximately 15 to 25%) and lower density of the cement binder phase. Typically, specific gravity of these concretes ranges from about 2.0 to 3.0. Dense refractory bricks reach somewhat higher values due to their lower porosity. Light-weight refractory concretes have specific gravities below 2.0, and would not appear to be suitable for gamma radiation shielding.

For LMFBR's, the biological shielding must be able to withstand sustained elevated temperatures in the range of 100 to 300°C, and possible transients up to 840°C (upset conditions), preferably without releasing water or reacting exothermically with molten sodium. With these requirements, several possible alternative systems show promise for shielding.

Dense refractory bricks made from tabular alumina, zirconia, or other dense refractory aggregates listed previously, most closely meet requirements for anhydrous shielding in LMFBR's. Their densities approach that of heavyweight concretes used in shielding for conventional light-water nuclear reactors. Their resistance to elevated temperatures and molten sodium has been demonstrated in tests and in service. If no mortar is used, a refractory brick masonry wall will contain no water, since the bricks are pre-fired to at least 1000°C during manufacture.

Concretes made with waterglass or phosphate binders and dense refractory aggregates may also make suitable shield walls in LMFBR's, if preheated to remove all water. Practically, this means heating to 100 to 350°C. Densities of these concretes are lower than that of densest bricks, due to higher porosities of castables.

Portland cement or HAC concretes using dense refractory aggregates may also be suitable for shielding in LMFBR's, if strong heating (600°C) under load or contact with sodium can be minimized or

avoided. Alternatively, these concretes could be pre-heated to 800 C to remove their water and meet the requirement of an "anhydrous" shield. However, even if heated to remove all water, portland cement concrete will still be susceptible to sodium attack, owing to the high silica content of cement paste.

Finally, the effects of gamma radiation on the materials discussed are not well-characterized, with the possible exceptions of ordinary portland cement concrete and zirconia. Effects of gamma radiation on mechanical and thermal properties would have to be determined before their suitability as shielding materials in LMFBR's can be evaluated.

D. Core Melt Isolation (above 870°C)

For total melt isolation with minor or no structural damage to the wall, the only possibilities are dense refractory brick linings and non-hydraulic concretes, especially the phosphate or magnesia concretes. These materials have been proven in industry for containing molten metals, molten steel in particular. Materials with proven resistance to molten sodium include:

- High density alumina brick
- High density magnesia brick
- Zirconia brick

In addition, some sodium resistance is reported for the following:

- Vitreous carbon or graphite brick
- High density fireclay brick (600°C)
- Fired waterglass-bonded corundum or tabular alumina concrete

For melts that do not exceed the temperature of about 1100°C, high alumina cement concrete with high quality refractory aggregates (corundum or tabular alumina), if previously fired, may also serve without undergoing significant chemical attack.

The degree of damage and disintegration of the wall by the action of the melt is however a design parameter of paramount importance. No doubt, a certain, perhaps very large, amount of damage may be allowed, possibly involving the disintegration of a layer of several

feet on the inside of the reactor containment wall or floor. During the disintegration process, the metallic melt gradually cools down. If it solidifies before the damage advances all the way through the wall, the goal of safe containment of the total melting of nuclear reactor core is achieved.

For this type of performance, normal portland cement concretes may prove to be satisfactory. This of course requires a careful determination of the depth to which the wall disintegrates, as well as various design measures already mentioned, including proper reinforcement, aggregate selection, steel fibers, lateral restraints, and transverse ties or anchors.

An important consideration is the limiting of the release of hydrogen resulting from reaction of sodium with water from the concrete. From this point of view, several measures may be taken to reduce water loss from the concrete. One method is to pre-dry normal portland cement concrete to remove free water, but not water of hydration within the concrete. Also many of the strategies cited should be used to control cracking. Cracking is undesirable since it provides additional surface area for chemical attack of sodium, and creates pathways for moisture within the concrete to escape.

The use of surface treatments (waterglass or magnesia) may also be useful in limiting hydrogen-producing sodium-concrete interactions by providing a chemically-inert, impermeable layer of material between concrete and sodium. This may reduce physical penetration, heating, and breakup of concrete, and also reduce the rate of (exothermic) chemical reaction between concrete and molten sodium. This possibility should be extensively investigated.

The use of fired refractory concretes, made with aluminous cements or non-hydraulic waterglass or phosphate binders, would eliminate the need for concern about water generation on heating from a sodium spill. However, this raises the unanswered question of how to practicably uniformly heat a monolithic reactor structure from temperatures on the order of several hundred up to 1000°C.

E. Summary

In suggesting the foregoing selection, primary attention has been given to material properties important for nuclear reactor structures; in particular good compressive and tensile strength, small thermal expansion, low creep and shrinkage, and, in certain situations, low susceptibility to sodium attack. Other properties, which may be of importance for other applications, have not been emphasized in this selection. These include resistance to large and numerous thermal cycles, abrasion resistance, and resistance to temperatures over 1000°C.

Section 4

PRINCIPAL GAPS IN KNOWLEDGE

Principal gaps in knowledge of material behavior needed to produce a reliable design of nuclear reactor containment structures are briefly outlined. For this purpose the basic materials already discussed are considered.

4.1 PORTLAND CEMENT CONCRETES

Present knowledge is incomplete in regard to the thermal and mechanical behavior of concrete exposed to sustained heat for moderate to long duration. Important properties data needed include: creep, the effect of moisture conditions and moisture migration upon creep, calculation of moisture migration, along with associated pore pressures and shrinkage deformations, the multiaxial properties of creep, and stress-strain relations in general. Also, very little is known about the fracture characteristics of concrete structures at elevated temperature, as well as the strain rate effects needed to evaluate the consequences of rapid loading. In addition, the thermodynamic relations for the equilibrium of pore water, and equilibrium pore pressures at elevated temperatures and various moisture contents, need to be studied. In addition, some sources suggest that temperature resistance of portland cement concrete can be greatly improved by using refractory aggregates. Very little material properties data exist for heat-resistant portland cement concretes.

When sufficient material properties data become available, identification and selection of promising materials for LMFBR applications can be made. Subsequently, testing of model or full-scale structural elements, made from selected candidate materials, should be conducted under conditions of load, restraint, and temperature comparable to those found in LMFBR's. Tests should be conducted under both service and accident conditions, where appropriate. Testing of this type will be needed both for preliminary evaluation of structural performance of selected materials, and also to serve as a "benchmark"

against which results of any future numerical structural analyses can be compared and evaluated.

Successful design will also require development of more realistic models for the prediction of thermal stresses in reinforced and prestressed concrete structures, especially those subjected to prolonged periods at elevated temperatures. The analytical model should account for effects of pore pressures, moisture migration as affected by the concrete thickness (size) and surface sealing conditions, as well as the effects of cyclic heating and very rapid heating (thermal shock).

The validity of such analyses could be determined by comparison with data from preliminary structural tests recommended previously.

The ultimate goal of the needed research should be the development of precise rules for the analysis and design of concrete structures for temperatures which exceed those currently permitted by codes for nuclear containments and vessels. Far higher service temperatures than the 150°F limit currently allowed by these codes are possible, but a better knowledge of mechanical properties coupled with much more realistic design and analysis procedures based on structural test data will be needed to allow higher temperature exposures.

4.2 HIGH ALUMINA CEMENT (HAC) CONCRETES

The knowledge of mechanical properties of HAC concretes at high temperatures is very limited. For some of these materials, not even the compressive and tensile strengths are known over the entire temperature range. Strength behavior of HAC concretes is complicated by the deleterious effects of conversion reactions (see Volume 1, Section 3.2.3). Because HAC loses much of its strength as a result of conversion reactions, it is not permitted as a substitute for portland cement in normal construction in the U.S. However, its residual strength after conversion may be sufficient for structural applications at elevated temperatures. Data on degree of strength loss due to conversion under conditions similar to those in LMFBR's are needed for material evaluation.

Furthermore, little is known of the effects of temperature on elastic modulus. Almost no data are reported on creep of these materials. Nothing is found in the literature on the migration of water in the pores of these materials, on pore pressures, or sorption isotherms. These are, however, not needed in case of a fired concrete where water has been driven out.

For high alumina concretes with tabular alumina aggregates, no data are available for hot compressive strengths, cold compressive strengths, or porosity before and after firing. For high alumina concretes with corundum aggregates no data exist on hot compressive strengths, on creep and shrinkage, and on porosity changes due to firing. For one promising candidate, namely the high alumina concrete with chamotte aggregate, sodium-concrete reaction tests apparently have not been carried out. Nothing is available on creep and shrinkage as well. For high alumina concretes with refractory lightweight aggregates, data are lacking on hot compressive strengths, on creep and shrinkage, porosity change due to firing, on Poisson's ratio, and on the resistance to thermal shock and spalling.

Mathematical models that have recently been developed for the deformation of normal concretes at high temperatures have at present no parallel in the case of refractory HAC concretes. Realistic designs would call for eventual development of models based on preliminary structural test data.

4.3 NON-HYDRAULIC CONCRETES

4.3.1 Phosphate-Bound Concretes

Knowledge of the mechanical properties of these refractory concretes is even more limited than that of high alumina cement concretes. Data on hot compressive as well as tensile strengths are lacking. Also, data on thermal conductivity, heat capacity, porosity or permeability changes due to firing, sorption isotherms at various temperatures, and moisture permeabilities are all unavailable in the literature. Further, at present no information on sodium-concrete reactivity is available. Information on volume stability of phosphate-bound aggregates is also limited. No creep data are reported in the literature, and for phosphate-bound lightweight

corundum aggregate concrete the coefficient of thermal expansion is also not given.

Non-hydraulic concretes generally have not been used for load-bearing structural applications. Data on structural behavior of these materials at room and elevated temperatures will be needed before their suitability for LMFBR applications can be assessed or modeled.

With regard to mathematical models needed for prediction of structural performance, the same comments can be made as for high alumina cement concretes.

4.3.2 Magnesia-Bound and Waterglass Concretes

Essentially the same comments can be made about these concretes as were made about phosphate-bound concretes.

4.4 REFRACTORY BRICK LININGS (MASONRY)

For these materials problems of design are somewhat different. The mechanical properties of refractory bricks are reasonably well known. The inelastic deformations, creep, and moisture sorption effects are relatively insignificant at temperatures below 600°C. The chief problem in design lies in determining the behavior of masonry structures. This behavior is strongly influenced by inelastic behavior of joints, the moisture absorption and diffusion properties, and possible chemical reaction of any joint binder material with sodium in the event of a sodium spill. Measurements of structural behavior obviously require relatively large specimens consisting of many bricks or blocks, which is an expensive proposition.

Nearly all construction practice in chemical processing industry is directly based on experience with refractory brick linings in vessels under service conditions. This experience cannot, however, be easily transplanted to the completely different situations in nuclear reactor structures. Some tests of large specimens consisting of many bricks would be highly desirable to determine irreversible deformations, response to multiaxial loading, creep, shrinkage, and thermal expansion.

However, many aspects could probably be determined using small-scale masonry models with bricks of a much reduced size. To some extent it should also be possible, and certainly much cheaper, to develop mathematical models for this behavior once the joint material behavior is well understood.

4.5 MATERIALS FOR RADIATION SHIELDING

On the subject of gamma radiation shielding, it should be noted that information on shielding characteristics of refractory concretes or brick systems is very scarce. Some data may be found for certain concrete components, such as zirconia or alumina minerals, however, shielding capability of most refractories has not been measured.

This does not mean refractories have no shielding capability. It may be that certain refractory systems incorporating dense aggregates are effective as primary gamma radiation shields. However, this will have to be established by future experimental evidence.

4.6 ADMIXTURES AND SURFACE TREATMENTS

Improvements in performance of castable materials for LMFBR applications may be realized by the use of various fiber admixtures or surface treatments. For instance, steel fibers are often added to refractory concretes used in furnace linings to improve resistance to structural cracking and increase liner durability. The use of steel or ceramic fibers may also offer improvements in performance of concretes for various LMFBR applications. The effectiveness of fiber reinforcement should be investigated as an adjunct to tests of concrete materials suggested previously.

Surface treatments are commonly used in concrete construction for severe chemical environments. Surface treatments are used to seal concrete surfaces. This reduces permeability and protect against attack from deleterious chemical reagents. It may be possible to improve resistance of portland cement or other concretes to sodium attack by using one of these surface treatments.

Materials used in surface treatment of portland cement concrete include sodium silicate (waterglass), magnesium oxide (MgO), carbon

dioxide, and various fluorides. (Vol. 1, Ref. 240). Their effectiveness as barriers to molten sodium are unknown, but should be investigated as part of studies of sodium resistance of concretes listed previously.

Section 5

RECOMMENDATION FOR FURTHER RESEARCH

Based on the preceding considerations an outline is given of some recommended further research. This work is needed to obtain sufficient additional material properties and structural behavior data to evaluate selected promising materials for LMFBR's, or other nuclear applications.

5.1 EXPERIMENTAL WORK

Phase A - Material Properties

Basic data on strength and deformation properties as a function of temperature are needed for most refractory concrete materials, particularly for non-hydraulic concretes. Effects of conversion reactions on strength and elastic properties of HAC concretes needs to be quantified. Values for residual strength at elevated temperatures need to be determined for assessment of suitability for structural applications in LMFBR's. Strength, fracture behavior, and deformation properties as a function of temperature are also needed for portland cement concretes incorporating refractory aggregates. In addition, effects of fiber reinforcement on concrete mechanical properties at elevated temperatures needs to be examined.

Further testing is needed on compressive, tensile, and triaxial strengths as well as fracture behavior under various thermal conditions (hot, cold, reheated, cyclic heating) and various moisture conditions (free moisture escape, both during and after the moisture escape, and where moisture is prevented from escaping). This needs to be supplemented by measurements of thermal expansion, shrinkage, and thermal properties during various typical temperature histories. This data is generally unavailable for refractory concretes, and very limited for portland cement concretes.

For nuclear structural applications, the triaxial stress-strain relations for selected materials, and their time and temperature dependence need to be known. The influence of temperature on strain-rate sensitivity of concrete stiffness also needs to be determined. Effects of moisture content on thermal and mechanical behavior and its variation, must also be determined. The knowledge in this area is incomplete for portland cement concretes, and completely lacking for high alumina cement concretes and other refractory systems.

It is therefore recommended that appropriate tests be conducted to determine deformation under constant uniaxial and triaxial stress states at elevated temperatures, measuring creep under sustained load. These tests should be carried out on a concrete that has lost its water due to heating and on concrete that was prevented from losing water (as in the case for concrete in the interior of a massive wall at the beginning of heating). Finally, tests should be made on concretes where water content is varied. These tests should be carried out in such a way that the effect of microcracking on the measured deformations can be eliminated and constitutive properties of these materials can be identified.

Refractory concrete or masonry, or portland cement concrete with refractory aggregates, have not reportedly been used for biological shielding from gamma radiation. Based on their high specific gravities, however, a number of dense refractory aggregates may prove effective in attenuating gamma radiation.

Dense refractory bricks may be the most effective system for "anhydrous" radiation shielding, but dried concretes made with water-glass or phosphate binders and dense refractory aggregates also look promising. Portland cement and HAC concretes may also be adequate if free water is removed by heating. Shielding capabilities of these concretes made from dense refractory aggregates should be investigated in comparison tests with normal weight and heavyweight portland cement concretes of the type currently being used for biological shielding in nuclear facilities. Promising refractory aggregates include: zirconia, silicon carbide, magnesia, chrome ore, and dense alumina (corundum or tabular alumina).

Molten sodium and molten core containment present the most severe environmental conditions to be faced by materials used in LMFBR's. Some data exists for molten sodium reactivity of various refractory concrete aggregates and masonry. However, data are needed on sodium resistance of liners made with refractory bricks using various mortars as binders, and also using dry joint construction. Also, very little data are available for refractory concretes. Tests of selected refractory concretes exposed to molten sodium at most severe temperature conditions (870°C) are needed. Tests should evaluate the effects on permeability of physical penetration by molten sodium. Also the resistance to chemical attack of the exposed material should be investigated.

Further, the possibility exists that sodium resistance of normal portland cement concrete or susceptible refractory concretes may be improved by use of surface treatments of concrete wall/floor assemblies. A number of surface treatments for concrete are currently used in severe chemical environments applications. These include: impregnation with waterglass, magnesia, or alumina, and treating concrete with carbon dioxide or various fluorides to harden and reduce permeability of the concrete surface. Effects of these surface treatments in limiting sodium-concrete interaction should be carefully studied.

Any improvement in sodium resistance of castable materials would provide greater flexibility in choice of containment materials and increase structural integrity under hypothetical accident conditions. Thus, surface treatments may provide a low-cost alternative to use of refractory masonry for adequate sodium containment and protection of containment structure. Tests could be conducted on portland cement concretes with and without surface treatments. Comparison tests could be made using refractory masonry materials.

Use of surface treatments for fired and unfired refractories may also be effective for enhancing resistance to sodium spills. However, no data is available on the effectiveness of these surface treatments for improvement of chemical resistance of refractory concretes. Treated and untreated refractory concretes should be tested under

sodium exposure conditions similar to those recommended above for portland cement concretes.

Phase B - Structural Performance

After material properties data are determined, it should be possible to identify and select promising materials for various LMFBR applications. It will then be necessary to evaluate the structural performance of selected materials under conditions simulating those found in LMFBR's, including load, restraint, and temperature.

Depending on the materials selected, the amount of structural testing needed will vary. Since much data already exist on ordinary portland cement concretes, structural testing needed would not be as extensive as for refractory concretes.

Tests should examine structural load capacity, deformation, shrinkage, expansion, and thermal properties of structural elements representative of those found in LMFBR's. Tests should be conducted under normal service conditions (sustained elevated temperatures), and also under upset conditions (transient heating or cooling), where appropriate.

Also, as mentioned earlier, the use of metal, glass, or ceramic fibers may be a useful method to improve the toughness and crack resistance of concrete for high-temperature applications. Testing of structures made from promising castable materials under high temperature exposures should include an assessment of the addition of fiber-reinforcement to improve high-temperature performance.

The purpose of structural testing is two-fold. First, it will be needed for preliminary evaluation of structural performance of selected materials. That is, structural testing is needed to determine if the promising material can be used to build a structure capable of performing adequately in an LMFBR environment. Second, results of structural testing, together with material properties data, can serve as the basis for numerical modeling of the response of the structure in an LMFBR. Structural tests data can be used as a "benchmark" against which results of numerical models can be compared and evaluated.

5.2 THEORETICAL WORK

Phase A

The theoretical work should be geared to determining the physical mechanisms of material deformation, cracking, failure, and fracture. Also the determination of a stress-strain relationship that can be used in numerical analysis of nuclear structures or supports is required. Considerable effort in this direction has already been made for portland cement concretes, but additional work is still needed. For example, a suitable time-dependent stress-strain relation (creep) under the conditions of variable moisture content and variable temperatures need to be determined. Existing tests and theoretical work are sufficient only for describing the behavior of dried concrete that has been allowed to freely lose its moisture upon heating.

For high alumina and other refractory concretes, work needed is much more extensive. Essentially all aspects of stress-strain and fracture behavior under short-time and sustained loads at high temperature and various moisture conditions have to be developed.

Subsequently, it is necessary to formulate analytical methods for the analysis of the effects of anticipated loadings and accident conditions on the structure. Such numerical or analytical methods would be based on stress-strain relations determined experimentally for portland cement or high alumina cement concrete. The methods should also account for the diffusion of moisture caused by heating of the structure.

Phase B

Of greatest practical importance is the development of clear and precise guidelines under which portland cement concrete structures can be allowed to be heated above 150°F. This limit is specified by the current ASME III-2 code (Vol. 1, Ref. 21). This code does not prohibit temperature exposures beyond 150°F, but states that the designer must when exceeding a temperature of 150°F, prove his design by adequate test data and special analysis. The rules for such an analysis should be developed such that the required individual steps for handling deformations, cracking or fracture,

spalling, effects of reinforcement, restraint, pore pressure and moisture movement, and other significant variables are specified.

The alternative use of refractory concretes or masonry for nuclear applications would require development of entirely different design procedures for high temperature exposure conditions. For these materials, it is unlikely that requirements of the current ASME code would be applicable.

Any proposed use of refractory systems in place of portland cement concrete in nuclear containment applications will require thorough experimental determination of material properties, and detailed analysis of structural behavior. Proposed design procedures developed for refractory systems would have to be verified by testing of structural components under conditions simulating the service environment. These steps would also be required for any design procedures for portland cement concrete containments operating above temperature limits imposed by the current nuclear code.

Comments on Research Direction

The preceding exposition involves a great amount of work to be done. Since the research funds are always limited, the choice of the best research direction is, therefore, extremely important.

In this regard, we should recognize that experimental work is normally much more expensive than theoretical work. For this reason, one should not embark on expensive testing where data could be collected from the literature, even if those data are not as perfect as one would desire. This is particularly important to keep in mind for portland cement concretes, for which rather extensive data already exists in the literature. Most of them are, however, not being used for designing structures for high temperatures, since the experimental results are not understood and have not been adequately explained with a coherent theory. In this area, the theoretical research might be more cost-effective. The first attempt should be to develop physically realistic and experimentally justified mathematical models of material behavior on the basis of the existing test data, before acquiring extensive additional test data.

With regard to model building, it should be remembered that only those models which explain the experimental evidence over its complete range and which are based on a rational and consistent concept of the physical mechanisms involved in the microstructure, are useful. Much too often, mathematical models and numerical simulations are being developed to explain only some data, disregarding others and neglecting to base the model on physical processes in the microstructure. There is little need for such models, even less than for duplicative material testing.

Section 6

SUMMARY

The present report analyzes existing knowledge on the use of concretes, especial refractory concretes, for nuclear reactor structures exposed to high temperatures, with particular reference to liquid metal cooled fast breeder reactors (LMFBR's). First, some basic properties such as strength, deformation capacity, thermal expansion, and insulating properties, as well as resistance to sodium attack, where available, were analyzed and compared for various concretes. Subsequently, advantages and disadvantages of these materials under various types of thermal exposure were summarized and discussed. Where comparative data were available these materials were ranked according to their performance in various situations. This led to identification of several materials that appear to be of greatest interest and potential for LMFBR applications.

From this analysis, which draws from information compiled in Volume 1, it was found that, for moderately high temperatures up to about 400°C, normal portland cement concretes appears to be a suitable material, provided that appropriate analysis and design procedures are developed. For higher temperatures, the use of high alumina cement concretes with certain types of aggregates appears to be a promising alternative material, provided that these materials can be prefired to develop ceramic bonds. The structure would best take the form of an assembly of fired blocks, plates or bricks fired above 1000°C, with joints that are either dry or made with a thin layer of refractory mortar. For very high temperature exposures, as well as for the conditions of sodium spill, use of refractory brick layers seems to be the most promising system.

The consequence of this analysis, and the principal gaps in existing knowledge, were identified and briefly outlined. The report was concluded by a recommendation for immediate research efforts.

In summary, it may be stated that normal portland cement concretes can serve at moderately high temperatures provided that proper design methods are developed. At very high temperatures or under conditions of sodium attack the use of refractory concretes as well as refractory bricks, and to some extent also portland cement concretes with refractory aggregates, appears to have a great potential.