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NUREG/CR-2279
SAND81-1732
R7
Printed March 1982

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Water Release From Heated Concretes

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Prepared by
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Albuquerque, New Mexico 87185 and Livermore, California 94550
for the United States Department of Energy
under Contract DE-AC04-76DP00789

MASTER

Prepared for
U. S. NUCLEAR REGULATORY COMMISSION

SF2900QA(8-81)

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Water Release from Heated Concretes

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Abstract

Water release from three concretes as a function of temperature has been determined experimentally. Limestone concrete releases more water at a moderate temperature than do magnetite or basalt concretes. The amount of water in the concretes is 6.2%, 6.3%, and 5% by weight for limestone, basalt and magnetite concretes respectively. All of the concretes show three distinct weight losses as a function of temperature. By 450K, 52 to 75 percent of the water is lost--all of the water is lost by 750-800K.

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TABLE OF CONTENTS

Introduction	1
Characterization of Concretes	
Limestone	1-2
Basalt	2-3
Magnetite	3
Experimental Results	
Weight Losses	4
Concrete Characterization Results	4-5
Discussion of Results	5-7
Conclusions	7
References	8
APPENDIX A: Chemical Compositions of the Concretes and the Concrete Constituents	18

TABLES

TABLE A - Limestone Concrete Mixing Ratio	2
TABLE B - Basalt Concrete Mixing Ratios	3
TABLE C - Magnetite Concrete Mixing Ratios	3
TABLE D - Strength of Concretes	5
TABLE E	5

FIGURES

Figure 1 - Limestone Concrete, Water Loss as a Function of Temperature	9
Figure 2 - Limestone Concrete, Percent Water Loss as a Function of Temperature	10
Figure 3 - Basalt Concrete, Water Loss as a Function of Temperature	11
Figure 4 - Basalt Concrete, Percent Water Loss as a Function of Temperature	12
Figure 5 - Magnetite Concrete, Water Loss as a Function of Temperature	13
Figure 6 - Magnetite Concrete, Percent Water Loss as a Function of Temperature	14
Figure 7 - Water Release Specimens	15
Figure 8 - Magnetite Concrete, Thermogravimetric Analysis	16
Figure 9 - Magnetite Concrete, Thermogravimetric Analysis	17

Introduction

Several types of concrete are used in the construction of nuclear reactors. Under certain postulated accident conditions, these concretes will experience temperatures beyond those encountered in normal operations. Concretes lose their mixing water when heated. This water is then free to react with other components of the reactor or to act as a source of pressure in the reactor containment. For example, molten sodium is used to cool the nuclear core of a fast breeder reactor. The attack of concrete by sodium is described in Reference 1. The molten sodium reacts with the water that is released from the concrete and forms hydrogen gas by reactions such as:

Therefore, the amount of water thermally driven from the concrete is important in analyzing sodium-concrete interactions. Several computer codes ^(2,3) exist that calculate the transient release of water from heated bulk concrete. However, these codes require a knowledge of the water available. To define the amount of water released at a given temperature, samples of basalt, limestone and magnetite concrete were obtained for water release experiments. Samples were also obtained to test for strength, specific gravity, absorption and voids in hardened concrete per ASTM standards.

Characterization of Concretes

Limestone

Limestone, being plentiful in the area, is proposed as the aggregate for the structural concrete in the Clinch River Breeder Reactor (CRBR). This particular limestone was 95% calcite, CaCO_3^* .

* The basic chemical composition of a number of concretes was determined by D. A. Powers. These compositions are given in Appendix A.

Samples of CRBR limestone concrete were made in accordance with the mix proportions established per ERDA (now DOE) letter dated 7/12/76.⁽⁴⁾ The mix ratio is given in Table A.

TABLE A
Limestone Concrete Mixing Ratio
(Kg/m³)

Cement	278.6
Water**	144.6
Sand	771.2
Aggregate	1079.4
Flyash	47.4
Air Entraining Agent	0.51
Water Reducing Agent	0.51

Basalt

Basalt concrete was used as a structural material in the Fast Flux Test Facility (FFTF). Basalt is made up largely of silicon dioxide, (SiO₂), calcium oxide (CaO) and aluminum oxide (Al₂O₃).

Samples of basalt concrete were made from "fine" aggregate (9.5 mm mesh) per ASTM C-33⁽⁵⁾ and ACI-613-54⁽⁶⁾. The mix ratio is given in Table B. The mix ratio was obtained from the FFTF project office.⁽⁷⁾

**The water content listed in the tables for each of the three concretes includes the water contained in the sand and aggregate as well as the added mix water.

TABLE B
Basalt Concrete Mixing Ratios
(Kg/m³)

Cement	258.7
Water	141.2
Sand (SiO ₂)	834.2
Aggregate	1073.3
Pozzalan	46.0
Air Entraining Agent	0.48
Water Reducing Agent	0.48

Magnetite

Magnetite concrete is found in the Fast Flux Test Facility (FFTF) reactor cavity region. This high density concrete is used as a "biological shield". Magnetite concrete, of course, contains largely the iron oxide, magnetite, Fe₃O₄. Magnetite concrete was made per ASTM C-33⁽⁵⁾ and ACI-613-54⁽⁶⁾. The mix ratio is given in Table C and was obtained from the FFTF project office.⁽⁷⁾

TABLE C
Magnetite Concrete Mix Ratios
(Kg/m³)

Cement	384.2
Water	189.2
Sand (Magnetite)	1373.4
Aggregate (Magnetite)	1757.6
Water Reducing Agent	0.94

For both the basalt and magnetite concretes, the aggregate and sand were purchased from the same commercial source that supplied construction materials for the FFTF.

Experimental Results

Weight Losses

The samples for dehydration studies were initially in the saturated, surface dry condition. Sample sizes ranged between 600 and 1200 grams. The specimens were cut (water/cooled) from the center portion of the cast cylinders and were air dried and stored at 100 percent relative humidity for at least 90 days. The specimens were used in the bulk form - not powdered. The samples were measured, weighed and then heated to an initial selected temperature. The samples were maintained at temperature until the difference between values obtained from two successive weighings was less than 0.5 percent of the lowest weight obtained⁽⁸⁾. The temperature was then raised to the next selected value.

The weight change of limestone concrete attributable to water loss on heating is shown in Figure 1 and the percentage change of initial water in Figure 2. Similar curves for basalt concrete are given in Figures 3 and 4 and for magnetite concrete in Figures 5 and 6.

In the water loss as a function of temperature figures, the free water (evaporable water)⁽¹¹⁾ is shown to be released relatively quickly between 300 to 350K. A slow release is evident then until a temperature of about 670K is reached from which point the remaining water (chemically constituted water)⁽¹¹⁾ is more rapidly released. The water released between 350K to 670K is defined in this report as, "chemically combined water." This water is more tightly bound than the free water but not as tightly bound as the chemically constituted water.

A typical basalt concrete water release specimen before an experiment is shown in Figure 7A. Figure 7B shows two limestone concrete specimens after they were subjected to a temperature of about 970 K and allowed to rehydrate at room temperature.

Concrete Characterization Results

Samples were also taken of all three concretes and stored at 100 percent relative humidity for compression tests at 7, 28, and 90 days. These results are shown in Table D.

TABLE D			
Strength of Concretes			
Time After Casting		Strength	
(Days)		MPa	psi
		(+2 percent)	
	<u>Limestone</u>		
7		25.9	3767
28		31.6	4590
90		35.2	5100
	<u>Basalt</u>		
7		12.9	1875
28		19.8	2865
90		27.1	3926
	<u>Magnetite</u>		
7		23.9	3468
28		40.4	5854
90		48.0	6962

The results of the tests for specific gravity, absorption, and voids in hardened concrete as per ASTM C642-75⁽⁸⁾ are shown in Table E.

TABLE E			
<u>Sample</u>	<u>Basalt</u>	<u>Limestone</u>	<u>Magnetite</u>
Absorption (%)	7.6	6.1	4.6
Specific gravity	2.7	2.6	4.0
Volume of Permeable Voids (%)	16.9	13.8	15.7

A thermogravimetric analysis⁽⁹⁾ (TGA) was conducted on a 54 mg sample of powdered magnetite concrete. The results of this analysis are shown in Figures 8 and 9.

Discussion of Results

Weight losses from concrete, as a function of temperature, consist of three events: 1) loss of evaporable water (300 to 350 K), 2) loss of chemically combined water (350 to 670 K), and

3) loss of chemically constituted water (670 to 750 K). (11)

In observing the curves of concrete water release as a function of temperature, one point is significant - limestone concrete releases more water at moderate temperatures than do magnetite or basalt concretes. For example, from Figure 1 it is seen that limestone concrete has lost about 80 kg/m^3 of water at 350 K. Figures 3 and 5 show that basalt and magnetite concrete have lost about 30 and 60 kg/m^3 of water, respectively, at 350 K. Water is found in concrete primarily in the cementitious phase. Each of the three types of concrete used the same cement, however, the limestone concrete had flyash added to retard the curing rate while the basalt and magnetite concretes used pozzolan.

The results found in these experiments are in general agreement with the results in reference 3. The data from reference 3 shows the quantity of water released was greater than the mixing water. Possible explanations are that the 6"x12" cylinders picked up additional water from the humid environment in which they were stored or that the moisture contained in the sand and aggregate was not included in the mixing water total. The former reason seems unlikely.

The strength of concrete has a large statistical variation both between types of concretes and between different samples of the same concrete. This is partly so because concrete is a composite, brittle material. The main contributors to concrete strength are the types of sand, aggregate and cement used as well as the water to cement ratio and the length of cure. The results of the strength measurements reported in the table are typical of their types and, therefore, lend support to the assumption that the results of these water release tests are representative of bulk construction concretes.

The TGA curves and the water release curves compare well. The curves have the same shape but are shifted along the x-axis. This is to be expected since thermal decomposition reactions typically obey kinetic expressions that describe the mass loss in terms of time, temperature and the amount of decomposing material present in the sample. The rate of mass loss is a function of both time and

temperature and consequently heating rate which was $10^{\circ}\text{C}/\text{min}$ in the TGA experiments. Varying heating rates will produce different amounts of mass loss at given temperatures. The magnitude of the difference depends on specific features of the decomposition reaction in question. As a rule, higher heating rates yield lower mass loss at a particular temperature as was seen in this study.

Conclusions

The term "concrete" describes a class of materials rather than a single material. The properties found within this class of materials can vary widely and depend on many factors. This study has shown that water release on heating follows this pattern. At the start of the study, this result was not anticipated--that one type of concrete would release more of its water under equilibrium conditions and at a given temperature than another type of concrete.

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Figure 1 Limestone Concrete, Water Loss as a Function of Temperature

Figure 2 Limestone Concrete, Percent Water Loss as a Function of Temperature

Figure 3 Basalt Concrete, Water Loss as a Function of Temperature

Figure 4 Basalt Concrete, Percent Water Loss as a Function of Temperature

Figure 5 Magnetite Concrete, Water Loss as a function of Temperature

Figure 6 Magnetite Concrete, Percent Water Loss as a Function of Temperature

A) Basalt Concrete Specimen
Before an Experiment

B) Two Limestone Concrete
Specimens After Water
Release Experiments and
Rehydration

Figure 7 Water Release Specimens

Figure 8 Magnetite Concrete, Thermogravimetric Analysis

Figure 9 Magnetite Concrete, Thermogravimetric Analysis

APPENDIX A*

Chemical Compositions of the Concretes and the Concrete Constituents

Oxide	Type I & II Cement	Limestone Aggregate	Limestone/ Common Sand Aggregate	Basaltic Aggregate	Sand	Fly Ash	Limestone/ Common Sand Concrete	Basaltic Concrete	Limestone Concrete	Expected Error
(Weight %)										
Fe ₂ O ₃	4.11	0.38	0.33	7.78	2.15	11.7	1.44	6.25	1.2	0.3
Cr ₂ O ₃	0.011	0.012	ND	0.06	0.042	0.022	0.014	ND	0.004	0.01
MnO	0.08	0.04	ND	0.08	0.02	0.02	0.03	ND	0.01	0.02
TiO ₂	0.2	0.04	0.05	1.82	0.18	2.24	0.18	1.05	0.12	0.04
K ₂ O	0.54	0.36	0.3	7.2	2.7	3.5	1.22	5.38	0.68	0.4
Na ₂ O	0.27	0.16	0.15	1.85	1.74	0.34	0.82	1.8	0.08	0.2
CaO	63.5	47.2	45.56	6.54	1.52	1.3	31.2	8.8	45.4	1.0
MgO	1.53	0.6	0.8	9.7	0.34	1.14	0.48	6.2	5.67	0.5
SiO ₂	20.1	8.0	13.0	54.9	82.8	51.2	35.7	54.73	3.6	1.5
Al ₂ O ₃	4.2	1.2	1.25	9.51	7.24	24.5	3.6	8.3	1.6	0.2
CO ₂	ND	38	40	<0.02	ND	ND	22	1.5	35.7	1.0
H ₂ O	ND	ND	ND	0.1	0.1	0.3	4.8	5.0	4.1	0.5
SO ₂	1.0	ND	ND	ND	ND	ND	<0.2	<0.2	<0.02	0.2

ND = not determined

*from reference 10

Acknowledgement

The author wishes to acknowledge
R. U. Acton, Division 1537, for
his helpful discussions and
technical advice.

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