SNO-STR-90-113

STATUS REPORT - BORONATED CONCRETE AND SULFURCRETE DEVELOPMENT

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Sept, 06, 1990

REPORT SNO-STR-

1. INTRODUCTION

Low activity concrete or sulfurcrete containing from 0.25 to 1.0% boron (wt%) is required in the waist region of the SNO cavity, for neutron and gamma shielding. Additionally, it is desirable that some boron loading be available for the backfill concrete, between the stainless steel liner and the rock and shotcrete concrete for the cavity dome. Previous work (1), has demonstrated that several boron compounds (eg. a boric acid, calcium hydroxide reaction product) can be added at the 1% boron level to low activity concrete (using a dolomite aggregate) to give a moderate strength concrete with a somewhat extended setting time. These boron compounds were found to be unsatisfactory for use in sulfurcrete.

This report outlines the development and testing of several high boron content glasses which can be added as a substitute for a portion of the aggregate to give both concrete and sulfurcrete of virtually normal strength, setting time and water resistance. These glasses should be excellent additives for the concrete backfill and shotcrete use, even where high strength is required.

2. MATERIALS SELECTION

The goal of this concrete prototype work was the preparation of normal concrete samples, using selected low-radioactivity portland cement, Haley dolomite aggregate, and a boron additive to enhance the absorption of thermal neutrons. In order to meet the design parameters used in recent shielding calculations, the concrete should have uranium levels of near 300 ng/g, thorium levels near 200 ng/g and an equivalent boron content of 0.25 % to 1.0 %.

A survey of Canadian Canada Lafarge cement plants was carried out in 1985 (2). Tests of samples of Portland cement from each plant, for thorium and uranium content, were carried out using neutron activation analysis. Using these results, Portland cement samples were obtained from the two Lafarge plants whose cements previously showed the lowest uranium and thorium content (plant # 9, 900 ng/g uranium (^{238}U), 3,300 ng/g thorium, plant # 14, 1,700 ng/g uranium, 700 ng/g thorium). Crushed dolomite from Timminco Ltd. Haley, Ontario was obtained for use as an aggregate. Borax (sodium tetraborate decahydrate - reagent grade), boric acid (crystal and powder - reagent grade), sodium tetraborate (anhydrous, fused-ground and in chip form) were used as sources of boron.

EXPERIMENTAL

3. BORON GLASS ADDITIVES

Glass can be formed from boron oxide B_2O_3 or silicon oxide SiO_2. Other oxides of sodium, calcium, aluminum, magnesium and lithium are common glass modifiers. Borax $Na_2O\ 2B_2O_3$ forms a glass; however, it is soluble in water causing the formation of $B(OH)_3$ which has deleterious effects on the set time and uniaxial compressive strength when included in a standard concrete. Glasses formed with SiO_2 are generally not water soluble. We have thus investigated the forming of a glass low enough in boron content and low enough in solubility, from a combination of silicon oxide and boron oxide, This glass could satisfy the boron content requirements while not degrading the properties of a standard concrete or sulfurcrete mix.

The silicon oxide glass forms a 3 dimensional skeleton based on the tetrahedron. The boron oxide glass forms a 2 dimensional lattice with each boron atom surrounded by 3 oxygen atoms and each oxygen connected to two boron atoms. In stable boron glasses, the 2 dimensional structure is apparently trapped in, or stabilized by, the 3 dimensional structure.

The glasses examined here were prepared in a furnace of the pyrometallurgy laboratory at Laurentian University, using 0.6 kg melts in a fire clay crucible. The charge was heated in air at 1350 deg.C for about 30 minutes, stirred with a stainless steel rod and

allowed to sit for another 30 minutes, then stirred just prior to pouring into 150 g size cones. The cones were crushed to < 1/4 size distribution in a jaw crusher.

Several mixing ratios for these glasses were investigated, using a 50% SiO_2, 50% Borax mix as the starting point. Eventually it was found that a 53% SiO_2, 43% Borax and 4% CaO glass was satisfactorily stable (under the tests performed to date) and competitive in cost. Compositions of glasses prepared and their stability are listed in Tables 1,2.

TABLE 1
GLASS MIXTURES

	Compounds	Oxides
1]	50% Borax	50% SiO_2
	50% SiO_2	34.5% B_2O_3
		15.5% Na_2O
1a]	remelt of above #1 glass.	
2]	53% SiO_2	53% SiO_2
	43% Borax	29.7% B_2O_3
	4% CaO	13.3% Na_2O
		4% CaO
3]	65% Corning 7070	52.39% SiO_2
	33% Borax	31.22% B_2O_3
	2% CaO	12.83% Na_2O
		1.5% Al_2O_3
		2% CaO
4]	Corning 7070 glass (labware)	
		80.6% SiO_2
		13.0% B_2O_3
		4% Na_2O
		2.3% Al_2O_3

TABLE 2

Test #1 Immersion in 95 deg.C distilled water for 24 hrs.

GLASS	% WT CHANGE	APPEARANCE
1]	62.5	white, crusty, flakey easily broken between fingers
1a]	37	partially affected, Still retains inner core of solid glass. Outer shell similar to glass #1 white flakey
2]	2.6	Still strong and clear only the surface is affected, slightly dull
3]	1.8	Similar to glass # 2 dull surface with some white specks.

2 PREPARATION

Batches of about 10 - 20 kg. concrete were prepared in a standard concrete mixer using standard construction methods (3). The weight % mix proportions are listed in Table 3. The boron additive was pretreated and then added to the concrete. during the mixing process. Standard test cylinders 3" in diameter and 6" in height were prepared by filling the molds 1/3 a time and rodding each layer 25 to 30 times into the previous third. Samples were allowed to set for 3, 7, 21 or 28 days depending on the requirements of the strength testing schedule.

TABLE 3 - SUMMARY OF CONCRETE BATCHES PREPARED

ALL INGREDIENTS GIVEN IN WEIGHT %

Batch and SAMPLE	CEMENT	WATER	AGGREGATE	ADDITIVE	FORM	W/C RATIO	BORON %
P1	18	9	73	Standard Concrete Mix Design			
A13	20	10	60	10	a,g	0.5	1.00
A14	23.4	21.3	49.7	6.6	b,d	0.9	0.70
A15	21.7	17.4	49.5	11.4	b,g	0.8	0.94
A16	19.2	13.1	57.8	9.7	a,d	0.68	0.96
A17	23.8	12.4	60	3.9	c,d	0.52	0.7
A18	21.6	10.4	63.7	4.2	c,d	0.48	0.7
A19	20	10	60.6	9.4	G3	0.5	1.0
A20	20	10	60.6	9.4	G5	0.5	1.0
A21	20	10	60.0	10.0	G6	0.5	1.0

CHEMICAL ADDITIVES

a Borax $Na_2B_4O_7 \cdot 10H_2O$

b Boric Acid H_3BO_3

c Sodium Tetraborate fused $Na_2B_4O_7$

d Calcium Hydroxide $Ca(OH)_2$

e Sodium Tetraborate chips $Na_2B_4O_7$

f Potassium Hydroxide 0.1 M KOH

g Calcium Oxide CaO

GLASS AGGREGATE

1 60% $Na_2B_4O_7$ 40% Silica fume

2 50% $Na_2B_4O_7$ 50% $Ca(OH)_2$

3 50% $Na_2B_4O_7$ 50%SiO_2

4 50% $Na_2B_4O_7$ 50% Quartz

5 50% $Na_2B_4O_7$ 50% Silica fume

6 43% $Na_2B_4O_7$ 53% SiO_2 4% CaO

7 65% Corning beaker glass (7070) 33% $Na_2B_4O_7$ 2% CaO

4. COMPRESSIVE STRENGTH TESTING

The uniaxial compressive test results were obtained from a Tinius Olsen press made available by the Civil Engineering Department at Laurentian University. The calibration is performed by the independent consulting firm "Calibration Canada" and is considered to be of high enough accuracy for the purposes of these tests. The test samples were capped with a compound such that the contact ends were parallel; this ensured that the force was evenly distributed over the entire cross sectional area of the sample. The methods used agree with CSA/ASTM regulations. The average strengths of the more successful batches are listed above. Currently, some glass loaded concrete test cylinders are being cured in air, and others in water at 40 deg.C, to assess the long term effects of the glass additive on the concrete. Negligible effects have been observed at 7 days. The strengths of the water-cured versus the air-cured samples are indistinguishable. The water-cured samples had small amounts of glass degradation only in the first 1 mm from the surface. Other samples from the same batch will be subjected to curing up to the 28 day test date. Note that the glass used in these tests (#1) represents a worst case scenario since this glass is the most soluble in hot water.

TABLE 4 UNIAXIAL COMPRESSIVE STRENGTHS

Batch	No. Samples	Curing Time	Uniaxial Compressive Strength (MPa)
P1	Normal concrete mix	28	28 + 2
A14	6	28	15.9 + 0.9
A15	5	28	18.2 + 0.9
A16	2	7	8.8 + 0.4
	1	14	11.31
	4	28	11.94 + 0.63
A17	9	28	
A18	8	28	
A19	4	7	25.8 + 2.5
A20	1	7	(A19 & A20 grouped in one test.)
A21	8	7	27.2 + 0.6

5. SULFURCRETE TESTS

A 0.5 kg sample of boron glass was sent to Dr. A Vroom (Sulfurcrete Products Ltd.) for addition to low activity (dolomite) sulfurcrete samples at a 1% boron level. Quoting from Vroom's report (4) (the glass) "behaves quite like any other aggregate in amounts up to at least 9.5%, by wt., of the total mix. We found no measurable swelling or solubility of the end product after soaking in hot water (80 deg.C) for 4 days.".

6. GLASS ADDITIVE COSTS

The cost of producing the borosilicate glass is not completely determined. An estimate from Timmins Testing Laboratories has been obtained for a pilot glass melt of 1 tonne at their facilities. This melt would be used to further define processing costs so that a projection to the 40 - 50 tonne order could be made.

1	Melt, crush, assay (flat rate)	$ 1600.00	
2	Borax (required for mixture # 2 Table 1) 1.75/kg or 19 bags @ 39.73/bag	$ 755.00	
3	Silica sand 530 kg @ 0.24/kg	$ 127.00	
4	Calcium oxide 40 kg @ 1.15/kg	$ 46.00	
5	Transportation (estimate)	$ 100.00	
	Total	$ 2628.00	($2.63/kg)

7. CONCLUSIONS

This study has demonstrated that low activity concretes, containing boron additives, can be prepared, using the standard approved construction techniques, from readily available materials. Concretes with boron glass loading up to 1% boron by weight with high strength are feasible. The use of glass containing up to 11% boron by weight appears to have little or no effect on the hydration process initial set occurs within 2-3 hours. These glasses have also been added to dolomite sulfurcrete at levels up to 1% boron without difficulty. Prototype sulfurcrete blocks are being prepared to verify this material and the production method. Further long term strength tests of concrete are also currently underway.

REFERENCES

1) E.D. Hallman, D.L. Cluff, Low Activity Concrete Preparation and Testing - an Update SNO-STR-90-52

2) Gündüz Güngör, Colemanite-Baryte Frit and Polymer Impregnated Concrete as Shielding Materials, Nuclear Engineering and Design, Vol. 72, pp 439-447, 1982.

3) Canadian Portland Cement Association, Design and Control Of Concrete Mixtures, 1984.

4) A. Vroom, Private Communication Aug 21, 1990