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HIGH DENSITY SLAG CONCRETE

T. E. Northup

(Thesis)

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ENGINEERING AND MECHANICAL DIVISION

HIGH DENSITY SLAG CONCRETE

T. E. Northup

(Submitted as a thesis to the Graduate Council of The University of Tennessee in partial fulfillment of the requirements for the degree of Master of Science)

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CHAPTER I

HIGH DENSITY SLAG CONCRETE

I. INTRODUCTION

"High Density Concrete Shielding" has become a widely used term where nuclear reactors and experimental cells are being designed and built, and one quickly discovers that these high density concrete shields are expensive. In comparison, normal concrete made with portland cement, crushed limestone, or similar aggregate is quite cheap if ample space for the shielding structure is available. When ample space is not available, thinner, but equal shielding must be provided by utilizing higher density concretes. Limited space is not the only justification for thin high density concrete shields. Special concretes are sometimes required to reduce the distance between operator and the process he must control within the shielded area. An important fact sometimes overlooked, or at least not thoroughly investigated, is that the use of shields made from high density concrete rather than from normal concrete can permit an overall building cost reduction by decreasing the size of the structure enclosing the shield, and by shortening the length of costly shield penetrations, manipulators, viewing windows, service lines, periscopes, control rods, shield plugs, etc. It can be emphatically stated, therefore, that economics plays a large role in the final selection of a shielding material. At the present time a concrete weight increase of 50 per cent is accompanied by a concrete cost increase of approximately

600 per cent for materials only. Methods of reducing such extreme cost increases are needed.

The search for a cheap, high density concrete led the Nuclear Foundation of Belgium to perform some experiments in 1961 using portland cement and a waste slag from the European metallurgy industry. A review of the Foundation's experimental test results[4] shows that the cheap waste slag concrete did compare favorably with the more expensive European barytes concrete in weight and shielding capacity. The major deficiency was that a concrete setting problem did occur when using fine slag; therefore, only coarse waste slag and fine barytes were used.

Mr. Jack B. Humphreys* recently completed a graduate thesis project at the University of Tennessee[2] on high density concrete using Ciment Fondu with high density and colemanite aggregates. The colemanite aggregate quantity that can be added to concrete made with portland cement is limited, as was the European slag, by its extreme effect on the concrete setting rate. Mr. Humphreys demonstrated that the setting rate was not seriously affected when colemanite aggregates were added to concrete made with Ciment Fondu.

These two developments, (1) a cheap high density waste slag, and (2) a cement that might overcome certain setting problems associated with the slag, provide a basis for the thesis work carried out and reported here.

---

*Assistant Professor Civil Engineering, Southwestern Louisiana Institute, Lafayette, Louisiana.

II. FEASIBILITY STUDY

Since costs play such a significant role in the selection of any material, initial investigation efforts were made to determine the feasibility of making waste slag concrete, its theoretical shielding capacity, and its cost as compared with concretes made with limestone, barytes, and magnetite aggregates.

Several hundred thousand tons of fine waste slag are available at a very reasonable cost from the St. Joseph Lead Company, Herculaneum, Missouri. By using the absolute volume of previously tested magnetite concrete mixes[3,8], theoretical waste slag mixes were calculated for pneumatic and conventional placement. Figures 1 and 2 show the cost versus unit weight aspects of the theoretical slag concretes as compared with limestone, magnetite, and barytes concretes. The specific gravity of the waste slag was reported by the St. Joseph Lead Company to be approximately 4.0 which is close to the magnetite and barytes aggregate specific gravities of 4.0 to 4.5. The slag concrete shown in Figure 1 contains only fine aggregate so that the concrete unit weight is less than the unit weights of the magnetite and barytes concretes which contain both coarse and fine aggregates.

A typical fine waste slag mechanical gradation, provided by the supplier, was plotted for comparison with the gradations of ASTM C-33, and with the gradations of the same magnetite fine aggregate used to compute the theoretical slag mix for pneumatic placement[3]. Both aggregate gradations are outside the ASTM recommendations for fine

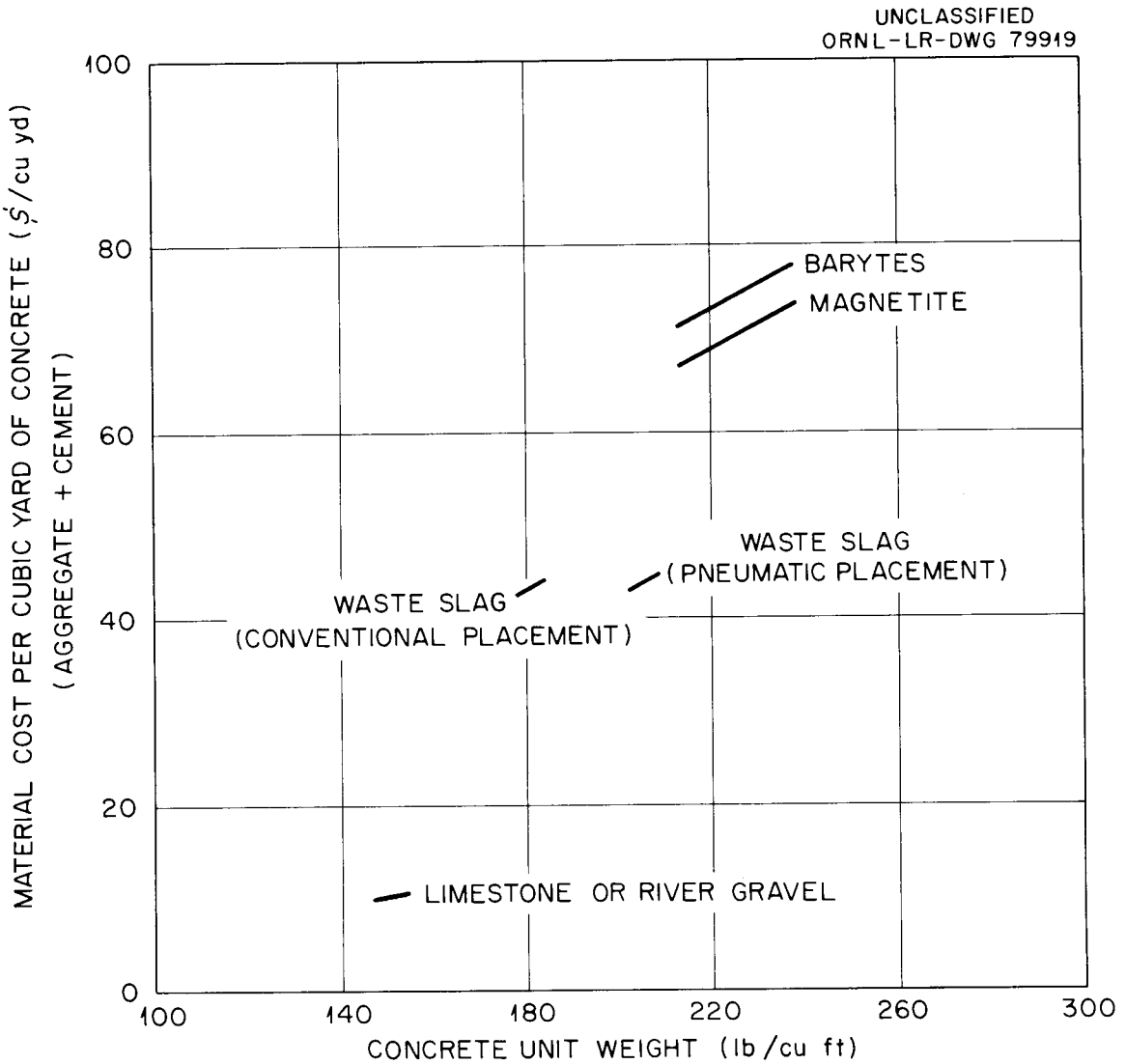


Figure 1. Material cost per cubic yard of concrete versus concrete unit weight.

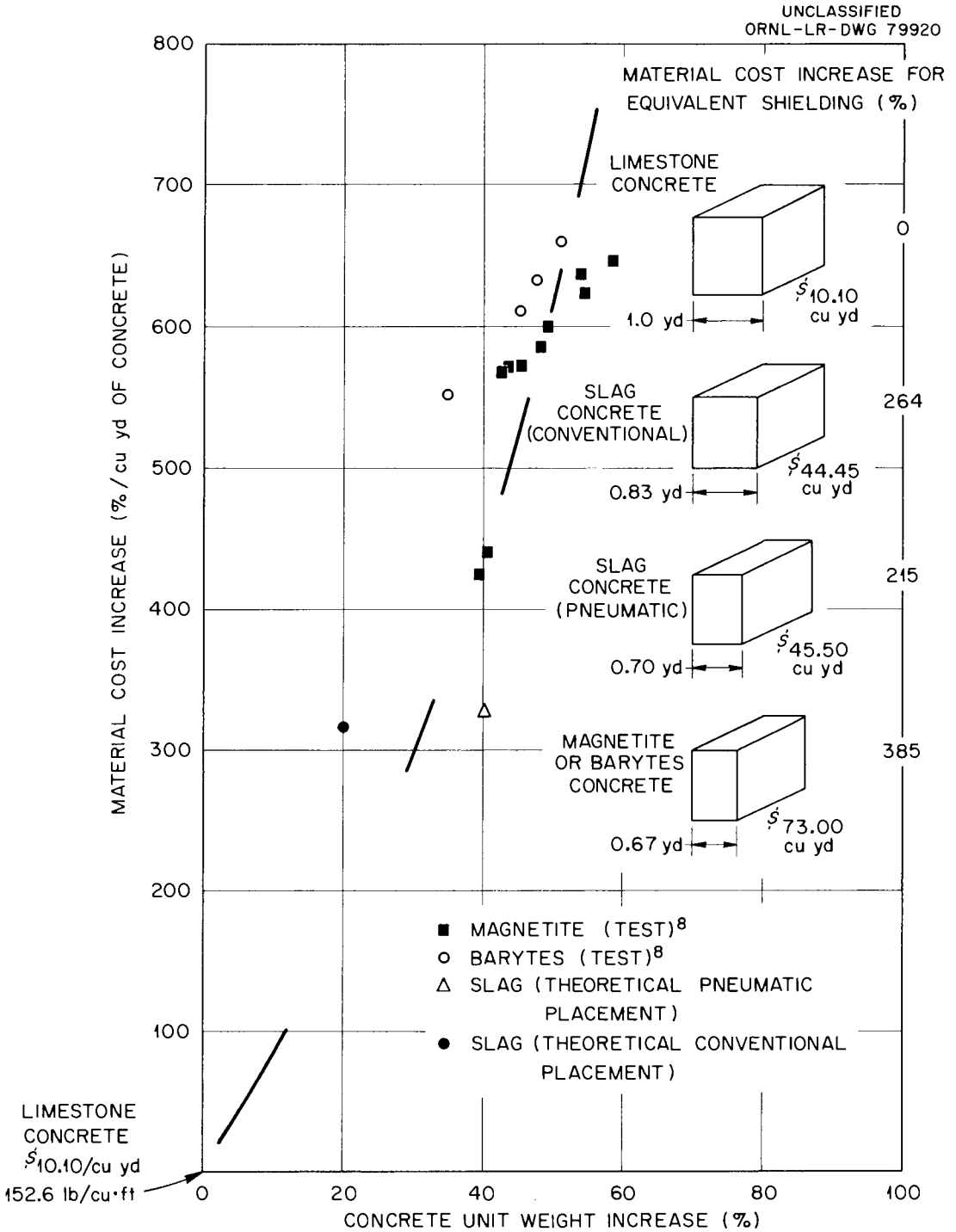
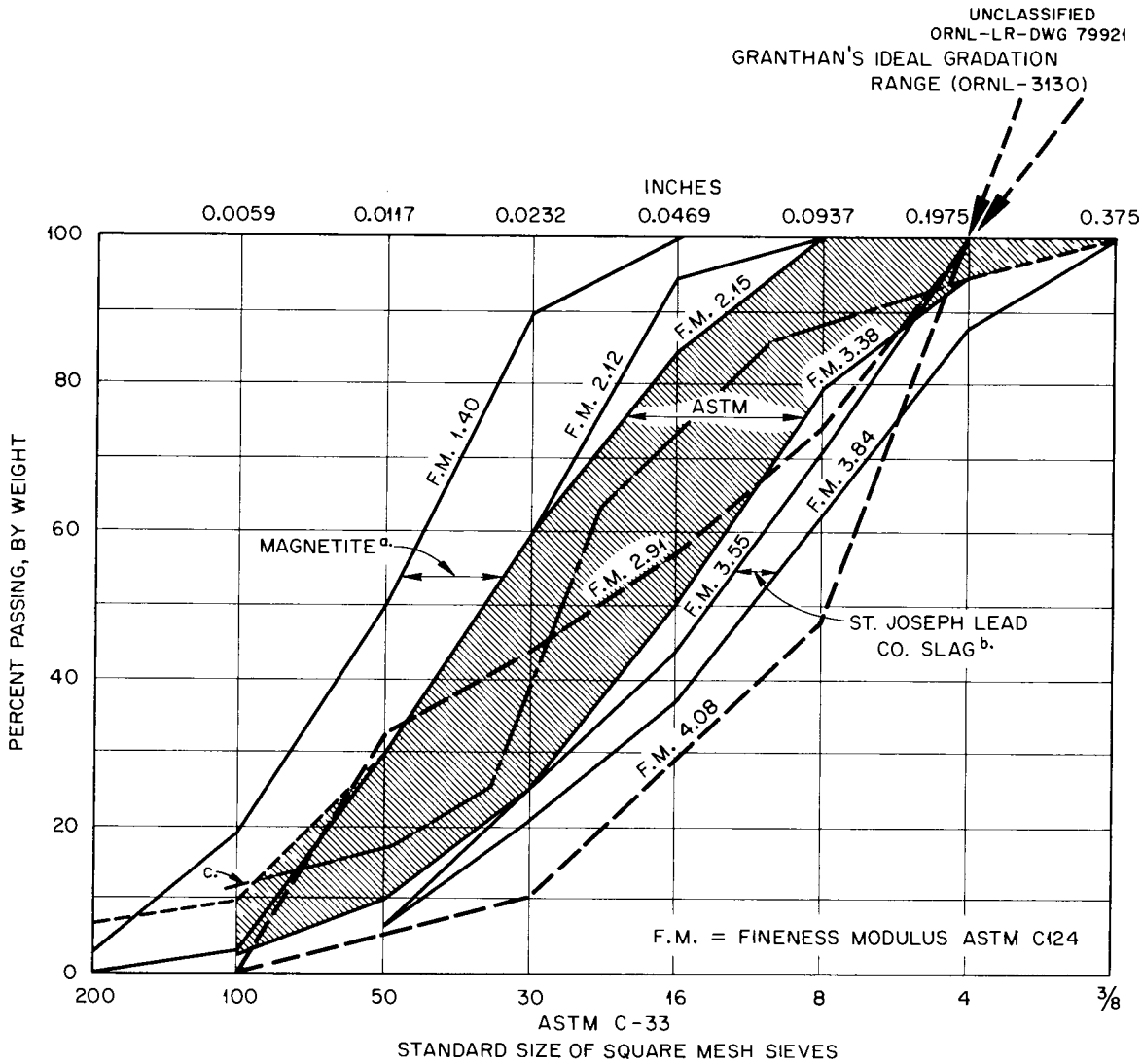


Figure 2. Material cost increase versus unit weight increase above that of limestone concrete.

aggregate to be used in regular limestone concrete. This condition exists because of the different particle sizes of the materials concerned. An ORNL report by W. J. Granthan[1] shows two extreme gradation curves for 1 1/2-inch maximum size high density aggregate required to obtain maximum density concrete depending on the cement-to-aggregate ratio used. The report also shows that these two curves can be used to mathematically produce similar gradation curves for 3/4-inch maximum size aggregate, 3/8-inch maximum size aggregate, etc. This curve-making procedure was employed to provide two extreme curves for the ideal gradation of No. 4 maximum size waste slag. These curves are all shown in Figure 3.

The theoretical slag mix for conventional placement has a cement-to-aggregate absolute volume ratio of 1.0:3.0 (see Table I). The ideal fineness modulus for such a ratio is 3.70 according to Figure 5 of Mr. Granthan's work for No. 4 maximum size aggregate. The waste slag gradation, as reported by the St. Joseph Lead Company, is within the gradation extremes with a fineness modulus close to the values theoretically desired, Figure 3.

It appeared that the slag, with all material greater than No. 4 sieve size removed, could be used to obtain maximum density concrete if the proper cement-to-aggregate absolute volume ratio were employed. (Granthan's curves were developed using a round-shaped barytes material. Caution must be used in applying the curves directly to sharp-cornered material such as the lead slag. The curves have been used as a guide only for this thesis.)



a. SPECIFIED GRADATION FOR HANFORD PNEUMATICALLY APPLIED SHIELDING CONCRETE (HWS-6452) MAGNETITE

b. GRADATION BASED ON LETTER FROM ST. JOSEPH LEAD CO. NOV 6, 1962, VALUES HAVE BEEN REVISED TO DELETE 1 in., 3/4 in., AND 3/8 in. MATERIAL

c. SLAG GRADATION OF BROKEN HILL PLANT, AUSTRALIA. THIS GRADATION ALSO EXPECTED FROM FUTURE ST JOSEPH LEAD CO. GRANULATION PROCESS.

Figure 3. Fine aggregate gradation comparisons.

TABLE I

THEORETICAL WASTE LEAD SLAG CONCRETE

Type of Construction: Pneumatic Placement[a].

Mix By Absolute Volume 1.1:1.0:5.2

Mix: lbs/cu.yd.		% By Wt.	Abs. Vol.	$/cu.yd.[b]
743	Ciment-Fondu (sp.gr. 3.20)	12.81	3.70	22.75
4,790	Fine Slag (sp.gr. 4.0)	82.75	19.20	22.75
257	Water	4.44	4.10	---
5,790		100.00	27.00 cu.ft.	$45.50

Unit Weight = 214.5 lbs/cu.ft. | At Mix[c].
3.44 sp.gr.

Type of Construction: Conventional Mixer[d].

Mix By Absolute Volume 1.9:1.0:3.0

Mix: lbs/cu.yd.		% By Wt.	Abs. Vol.	$/cu.yd.[b]
920	Ciment-Fondu (sp.gr. 3.20)	18.87	4.61	28.20
3,420	Fine Slag (sp.gr. 4.0)	70.00	13.69	16.25
543	Water	11.13	8.70	---
4,883		100.00	27.00 cu.ft.	$44.45

Unit Weight = 181.0 lbs/cu.ft. | At Mix[c].
2.90 sp.gr.

a. Mix derived from data in Reference 3.

b. Material costs only, F.O.B. Oak Ridge, Tennessee.

c. Density decrease after prolonged curing will be less than concrete made with portland cements since higher percentages of water combine with the Ciment Fondu (see Figure 14).

d. Mix derived from data in Reference 8.

The feasibility of obtaining a satisfactory slag concrete was explored by making a small preliminary mortar mix to observe the setting characteristics of the slag and cementing agent. Both portland and Ciment Fondu were used separately with fine waste slag in a measured volume ratio of 1.1:1.0:5.0 (water, cement, slag). The portland-slag mix crumbled at touch at twenty-four and forty-eight hours. The Ciment Fondu-slag mix could only be broken by using a hammer at forty-eight hours. This simple test gave encouraging results.

The shielding capacity of waste slag concrete is described by two values; the total linear attenuation coefficient (μ = cm^{-1}) for gamma radiation and the effective removal cross section for neutron radiation (Σ_r = cm^{-1}). These values were computed using the typical chemical analysis of the waste slag shown in Table II, and the theoretical mix for conventional placement shown in Table I. The results of these calculations are shown in Table III along with typical barytes and magnetite mass attenuation values for comparison.

The various major chemical elements in the waste slag stay within a narrow range as shown in Table II. The chemical analysis of the slag was obtained from the St. Joseph Lead Company plant production control records. Most elements are reported either daily or weekly as indicated. The slag analysis was deemed representative enough to provide a basis for the initial investigations in shielding capacity. The Ciment Fondu chemical analysis was obtained through correspondence with the Lafarge Aluminous Cement Company, Limited, London.[7]

TABLE II

THEORETICAL COMPOSITION OF WASTE LEAD SLAG CONCRETE

Source		Typical Chemical Analysis[a.]	%	Element	% by wt. in Compound	% by wt. of Element in Mix[b.]
Ciment Fondu[c.]	Lafarge Aluminous Cement Co., Ltd., London, Eng.	Al_2O_3	39.0-40.0	Al	20.9	3.94
		CaO	36.0-38.0	Ca	26.4	4.98
		Fe_2O_3	9.0	Fe	11.0	2.08
		FeO	6.0	Si	2.1	.40
		SiO_2	4.0-5.0	Ti	1.2	.23
		TiO_2	2.0	Mg	.6	.11
		MgO	<1.0	S	.04	.008
		SO_3	0.1	K	.04	.008
		K_2O	0.05	Na	.07	.014
		Na_2O	0.10	O	36.9	6.96
		Unknown	-	-	.75	.14
					100.00	18.870
Waste Lead Slag	Herculaneum, Mo.	Insol (Sulfides)	2.0-3.0	Sulfides	2.5	1.75
		[d.] PbO	1.5-3.0	Pb	1.96	1.37
		[d.] FeO	28.0-35.0	Fe	24.55	17.19
		SiO_2	22.0-26.0	Si	11.20	7.84
		[d.] CaO	8.0-14.0	Ca	7.85	5.49
		[e.] MgO	4.0-5.0	Mg	2.71	1.90
		[e.] Al_2O_3	5.0-7.0	Al	3.18	2.23
		[d.] ZnO	10.0-12.0	Zn	8.85	6.20
		[e.] Cu & S	Traces	O	29.95	20.95
		Unknown	-	-	7.25	5.08
					100.00	70.00
H_2O				H	11.18	1.24
				O	88.82	9.89
					100.00	100.00

Elemental Composition of Concrete (Sp.gr. 2.90)		
Elements	% by wt.	g/cm³
Fe	19.27	.558
Si	8.24	.239
Pb	1.37	.040
Al	6.17	.179
Ca	10.47	.303
Ti	.23	.007
Mg	2.01	.058
Zn	6.20	.180
S	.008	-
K	.008	-
Na	.014	-
H	1.24	.036
O	37.80	1.098
Unknown	5.22	.151
Sulfides	1.75	.051
Total	100.00	2.900
H_2O @ Mix	11.13	.323
H_2O[f.]	3.68	.107
H	.41	.012
O	3.27	.095

a. The total iron oxide content of Fondu hardly varies but the proportion of ferric to ferrous oxides may vary appreciably.

b. Based on % by wt. of compound in concrete. See Table I.

c. Material obtained from warehouse, Savannah, Ga.

d. Daily analysis checked by St. Joseph Lead Co.

e. Weekly analysis checked by St. Joseph Lead Co.

f. H_2O retained after curing (based on Figure 14, 50°C).

TABLE III

WASTE LEAD SLAG CONCRETE SHIELDING COEFFICIENTS

Sp.gr. = 2.90
Absolute Volume Ratio: 1.9:1.0:3.0 (Water-Cement-Slag)

Element	Atomic Wt	$\rho(gm/cm^3)$[a.]	Neutron Attenuation[b.]		γ-ray Attenuation for 6 Mev[c.]	
			$\frac{\Sigma_r}{\rho}(cm^2/gm)$	$\Sigma_r(cm^{-1})$	$\frac{\mu}{\rho}(cm^2/gm)$	$\mu(cm^{-1})$
Fe	55.850	.558	.0200	.0112	.0305	.0170
Si	28.060	.239	.0295	.0071	.0278	.0066
Pb	207.210	.040	.0092	.0004	.0446	.0018
Al	26.970	.179	.0301	.0054	.0265	.0048
Ca	40.080	.303	.0240	.0073	.0303	.0092
Ti	47.900	.007	.0210	.0001	.0287	.0002
Mg	24.320	.058	.0320	.0019	.0268	.0015
Zn	65.380	.180	.0180	.0032	.0316	.0057
S	32.066	--	.0275	--	.0287	--
K	39.100	--	.0230	--	.0291	--
Na	22.991	--	.0330	--	.0255	--
H	1.008	.036	.6020	.0217	.0449	.0016
O	16.000	1.098	.0410	.0449	.0255	.0279
				.1032		.0763

	$\Sigma r/\rho$	μ/ρ
Waste Lead Slag Concrete (Sp.gr. 2.90)	.0356	.0263
Barytes Concrete[d.] (Sp.gr. 3.30)	.0301	.0306
Magnetite Concrete[d.] (Sp.gr. 3.29)	.0299	.0282

a. Values from Table II.

b. $\frac{\Sigma r}{\rho}$ values are taken from Reference 9.

c. $\frac{\mu}{\rho}$ values are taken from Reference 11.

d. See Reference 9, page 41. See Reference 10, pages 25 and 26 (BA-OR and M-HW1).

The above feasibility reviews on cost, theoretical mix, setting characteristic, and shielding capacity provided a basis for proceeding with laboratory experiments.

CHAPTER II

MATERIALS: WASTE LEAD SLAG, CIMENT FONDU, PORTLAND CEMENT, CALCIUM CHLORIDE, AND WATER

I. WASTE LEAD SLAG

Slag material for experimental purposes was offered by the St. Joseph Lead Company. A visit to the slag source in Herculaneum, Missouri, in November 1962, was made to evaluate availability, handling methods and equipment, shipping methods and limitations, quality variations, price stability, and to acquire approximately one ton of representative waste slag.

Availability

The waste slag available for sale is based on the amount of produced slag which is not used as a dilutent in the main plant operation. A flow diagram is shown in Figure 4. Two furnaces are normally operated; therefore, approximately thirty-two tons of waste slag are produced daily. The company officials estimate that over a million tons of material are stacked around the plant site.

Handling Methods and Equipment

The slag is taken out of the furnace by being tapped off at a certain elevation of the molten ore load in the furnace and dumped into steel buckets on wheels. The buckets are pushed out to an area where the molten slag is dumped into a half-round steel trough. A jet of water is

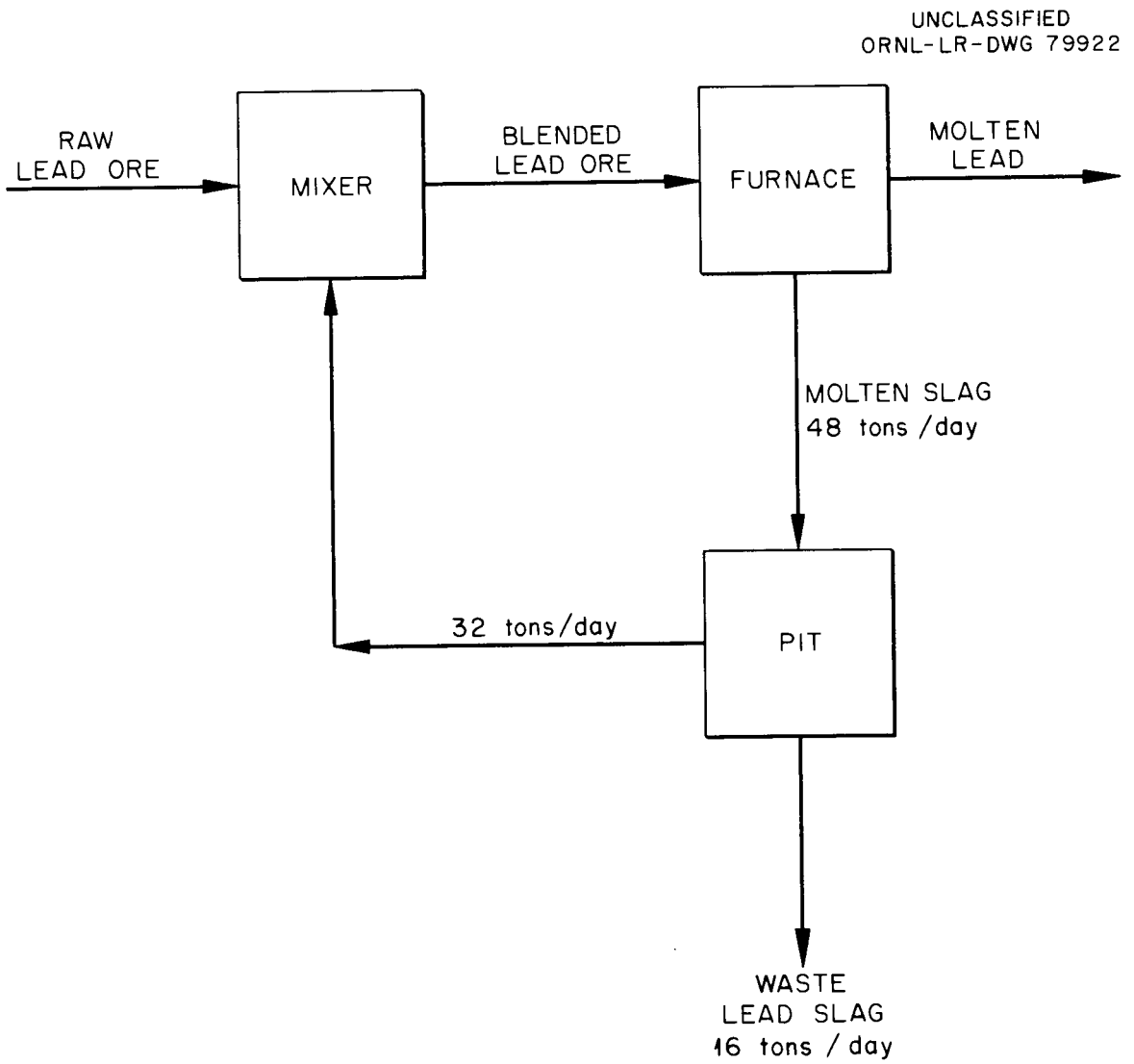


Figure 4. Waste lead slag production flow diagram.

forced along the trough at the same time to granulate the molten slag into fine particles by rapid cooling. By regulating the rate of water flow the size of the particles can be fairly well controlled: fast flow--small particles; slow flow--particles up to one (1) inch sieve size. The granulated slag slides into a pit where it is subsequently loaded into drop-bottom gondola rail cars. These cars are taken to the incoming raw lead ore staging area where the slag is mixed with the raw ore to reduce the lead content entering the furnace to about 50 per cent. Maximum furnace efficiency is obtained at this percentage. Surplus or waste slag goes to a waste slag pile. Drag-line cranes on rail cars perform the slag loading chores.

Shipping Methods

When slag is to be shipped, the slag that was dumped at the waste site is loaded by the freight company and this cost consequently becomes a part of the rail freight charge from Herculaneum, Missouri, to the job site. Weather offers no problem for rail shipments since loading operations can be carried out at all times of the year. Most rail shipments would be by open gondolas. The slag does not seem to break up because of handling although the larger clusters of fine particles that were not completely granulated do eventually break down during handling operations. Bags or barrels would not normally be used or required for shipping the slag and special handling charges would be added if gondolas were not used for all shipments.

In determining whether shipments should be made by barge, the following items should be considered even though the Mississippi River does go by the "back door" of the plant:

Trucks must be loaded at the waste slag site and unloaded at the barge site approximately one-fourth mile away.

Special river derricks on a separate barge must be used to clam-shell the ore from the bank to the ore barge.

River elevations vary by thirty-five feet making loading uncertain at times although these periods seldom last more than a couple of weeks.

For these reasons, barge shipment is not recommended by the St. Joseph Lead Company.

Quality

The waste slag does not appear to vary appreciably in size. Several years of storage have shown no noticeable deterioration. The granulation process will be more carefully controlled as the result of new equipment now being installed at the lead furnaces. The particle sizes produced should then fall within the ASTM fine aggregate limits. (A plant run by the Broken Hill Associated Smelters Proprietary, Limited, Port Piere, Australia, is now producing slag by a similar method and the typical gradation is shown in Figure 3, subscript c.)

Screening. Size 3/8 inch, and down, sieves are available at the plant although the equipment is seldom used. Air classification can be provided to remove excess fines if required.

Crushing. Some old unused equipment is available at the plant and it could be re-activated. This probably would add appreciably to the cost of the waste slag.

Fines. The new granulation process will produce more fines than the present process does. The percentages below the No. 100 sieve size do not exceed the ASTM allowable values; therefore, no "dust" problems should be encountered with slag produced by either process.

Impurities. The exposed surfaces of the waste slag storage piles showed considerable amounts of dirt and dust which was evidently caused by long outdoor storage rather than by slag deterioration. Slag deterioration due to weathering appeared to be nonexistent.

Density Variations With Size

The St. Joseph Lead Company did not have this information although they report the waste slag as having a 4.0 specific gravity.

Fineness Modulus

This value was not available from the St. Joseph Lead Company.

Unit Density

Furnished by the St. Joseph Lead Company as 130 pounds per cubic foot.

Price Stability

Approximately one million tons of waste slag are available with thirty-two tons being added to the waste pile during each day of plant operation. (Plant operates 365 days a year, 24 hours a day.) This slag is frequently given to railroad companies and the Missouri Highway Department for ballast and fill free of charge. There seems to be little danger of a price increase for the slag even if the slag is used for high density concrete. The St. Joseph Lead Company offers a loading price at Herculaneum, Missouri, of $2.90 per ton (two thousand pounds). They indicate that rail shipment to Oak Ridge will add approximately $6.60 per ton to the waste slag cost, or $9.50 per ton F.O.B. Oak Ridge, Tennessee. The slag carries the lowest rail classification, "waste". The St. Joseph Lead Company rail quote is based on average costs for similar material shipments into the Knoxville area. Land Grant rail shipment reductions have not been considered in these estimates but should be if a large order for slag is placed.

Miscellaneous

The total lead smelting process was reviewed to determine if another high density material existed that might be suitable for concrete work. Results:

1) Raw lead ore was not uniform in density.
2) A "mat" from lead furnaces exhibited good density but costs of $80 per ton due to valuable chemical properties limit its use.

Approximately 2,300 pounds of waste slag was obtained free of charge for experimental use to determine if high density concrete could be made. St. Joseph Lead Company has made concrete using lead powder concentrates but not the waste slag.

Physical Property Experiments

The slag sample material obtained at Herculaneum was tested at the Concrete Testing Laboratory, University of Tennessee, to determine several physical properties including: (See Appendix A for test methods employed)

Mechanical analysis

Specific gravity and absorption

Material finer than No. 200 sieve

Unit weight

Voids in aggregate

The slag mechanical gradation limits for the samples obtained are portrayed in Figure 5, and the experimental average gradation shown was used for all subsequent concrete tests. Other slag physical properties are shown in Table IV. The material greater than a No. 4 sieve, approximately 20 per cent of sample, was discarded after specific gravity and absorption tests were completed. Emphasis was placed on material passing a No. 4 sieve for two reasons. First, the larger the slag size the lower the specific gravity (Table IV). The large aggregate is made up of clusters of finer material lightly fused together as a result of improper

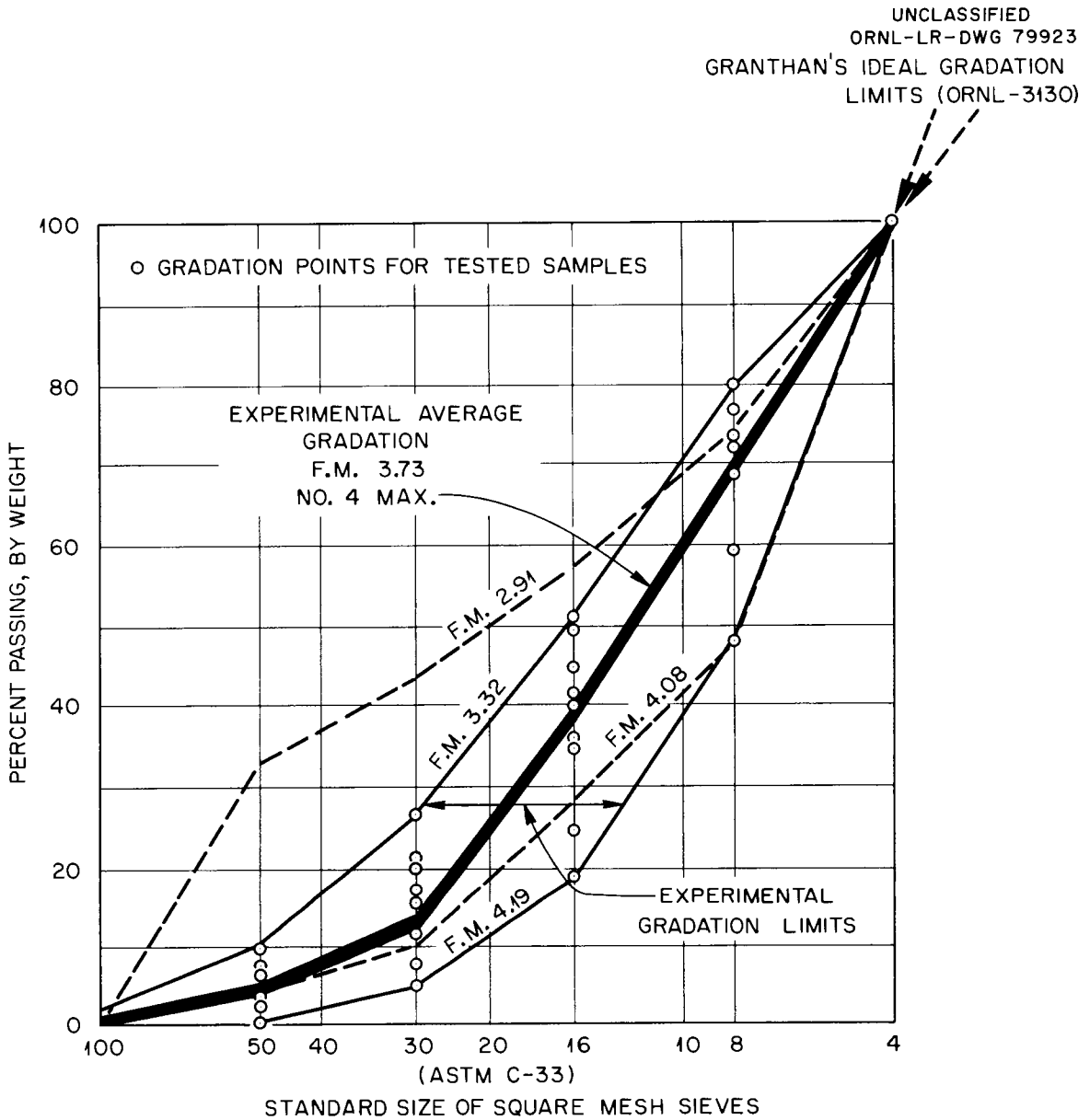


Figure 5. Waste lead slag gradation limits compared with theoretical limits for maximum concrete unit weight.

TABLE IV

WASTE LEAD SLAG PHYSICAL PROPERTIES

		Material Size					
		Waste Lead Slag[a]	Coarse	Fine			
			Above No. 4	- No. 4 + No. 8	- No. 8 + No. 16	- No. 16 + No. 30	- No. 30 + No. 50
1.	Bulk Specific Gravity	3.80	3.73	3.86	3.86	3.83	3.97
2.	Bulk Specific Gravity (Saturated Surface - Dry Basis)	3.82	3.79	3.91	3.90	3.85	3.92
3.	Apparent Specific Gravity	3.87	3.97	4.05	3.99	3.91	3.99
4.	Absorption (%)	.44	1.64	1.16	.83	.50	----[b]
5.	Unit Weight #/cu. ft. (Dry Rodded)	137.00	112.00				
6.	Unit Weight #/cu. ft. (Vibrated)	140.00					
7.	Fineness Modulus	3.73					
8.	Specific Heat - Solid Slag (cal/gm/°C)[c]	0.16					
9.	Organic Impurities	None					
10.	Voids in Slag (%)	41.00					
11.	Material Finer Than No. 200 Sieve (%)	0.3 to 0.5					

a. Average graduation (F.M. 3.73 Figure 5)

b. Erratic results all < 1.00 per cent

c. Furnished by St. Joseph Lead Company

water cooling during the granulation process. These clinkers do not pack together, and their shape prevents smaller sized aggregates from filling the voids. Second, experience has shown that fine aggregates, such as magnetite, can be used to make dense concrete by using pneumatic placement equipment. Such fine aggregate concretes have proven to be denser than those placed by conventional methods.[6] With this in mind, the waste slag investigation was carried out so that the material could be used for conventional or pneumatic concrete placement.

The specific gravity and absorption values for the waste lead slag (Table IV) turned out to be lower than the values determined for the individual fine slag sizes. Surface characteristics of the slag provide a possible explanation. The granulation process (see page 13) leaves the surface of the slag poc-marked with small indentations which hold water easily by surface tension. The absorption test, described by ASTM C-128-59, requires that the material be brought to a saturated surface-dry condition before a sample is weighed for testing. It was noticed that the surface-dry condition could be reached even though the slag indentations held water. Therefore, the finer the material the fewer the water-holding indentations and the lower the absorption percentage. When the slag with all sizes combined was tested, the lowest absorption value was obtained (.44 per cent). Since the sample contained large and fine material, one might assume that an average absorption value would be obtained. An average value was not obtained due to the time required for the sample to reach the saturated surface-dry condition. The coarser

material, between a No. 8 and No. 4 sieve, required about thirty minutes to reach the proper test conditions, whereas the combined material required about two hours. This additional time permitted the water held in the coarse slag indentations to evaporate.

Essentially the same argument can be presented to support the low specific gravity values for the slag sample with all sizes of material combined. All specific gravity calculations contain the expression (V-W) in the denominator of the equation,

where

V = Volume of flask

W = Quantity of water added to flask

Since the saturated surface-dry sample contained little trapped water, more slag was introduced into the flask which reduced the quantity of water needed to fill the flask. As (V-W) increases, the specific gravity decreases.

A slag specific gravity of 3.80 was used in all of the computations for the concrete testing work.

II. CIMENT FONDU

The Ciment Fondu Lafarge Corporation, New York 11, New York, furnished cement material out of their Savannah, Georgia, warehouse for the experimental work. Since little technical data on Ciment Fondu were readily available, a query to the London office of the Lafarge Corporation produced several interesting points and references concerning the calcium aluminate cement.[7]

Chemical Composition

The chemical composition of Ciment Fondu differs considerably from that of portland cement. This difference is shown in Table V along with Atlas Lumnite, a high aluminum cement produced by the Universal Atlas Cement Company, Division of U. S. Steel, here in the United States.

Ciment Fondu should not be mixed or stored with portland cements since flash setting can occur. Additional data on the phenomenon of flash setting can be obtained in Reference 12.

Weight

The weight of loose, bulk, dry Ciment Fondu for the purposes of mixes measured by volume is 94 pounds per cubic foot (one sack). The weight of a cubic foot of cement loosely filled into a measure is about 85 pounds, whereas the weight of tamped cement may be as high as 118 pounds per cubic foot. This weight is about 2 to 4 pounds more than a cubic foot of portland cement in the same state of compaction.

Specific Gravity

The specific gravity supplied by the Lafarge Corporation for the loose, bulk, dry Ciment Fondu is 3.20 to 3.25. A value of 3.20 was used in all of the computations for the concrete testing work.

Cost

Ciment Fondu purchased in 70,000-pound lots can be obtained at approximately $2.88 per sack, F.O.B. Oak Ridge, ($.0306 per pound) which

TABLE V

TYPICAL CEMENT CHEMICAL COMPOSITION COMPARISONS

Element	Ciment Fondu (% by wt.)	Atlas Lumnite (% by wt.)	Portland Type I (% by wt.)
Ca	26.4	26.20	47.9
Al	20.9	22.40	3.1
Si	2.1	3.93	9.7
Fe	11.0	7.92	1.8
Mg	.6	.72	1.8
S	.04	.07	.4
O	36.9	38.24	35.3
Ti	1.2	Included with Fe	---
K	Traces	---	---
Na	Traces	---	---
Insoluble Residue	.86	.52	---
	100.00	100.00	100.00

is about three times the cost of Portland Type I. A similar purchase of Atlas Lumnite would cost about $3.25 per sack. The price difference between the English and American high aluminate cement provides an interesting picture of foreign competition.

No laboratory tests were performed on the Ciment Fondu material alone. Atlas Lumnite cement was not used in any of the concrete testing work.

III. PORTLAND CEMENTS

Portland - Type I and Type III

Hydraulic cements manufactured by the Volunteer Portland Cement Company, Knoxville, Tennessee, were used. The specific gravity was taken as 3.15, the usual value for these cements. Portland cement, Type I, can be purchased at approximately $1.10 per sack F.O.B. Oak Ridge ($0.0117 per pound).

IV. CALCIUM CHLORIDE

Solvay Calcium Chloride supplied by the University of Tennessee, Engineering Experiment Station, was used as an accelerator to shorten the initial setting time of concrete batches made with portland cements. Flake form calcium chloride, not exceeding 2 per cent by weight of cement, was used. Supplemental data on the use of calcium chloride can be found in Reference 13.

V. WATER

Plain tap water was used for all experimental work performed at the Concrete Testing Laboratory, University of Tennessee.

CHAPTER III

MORTAR TESTS

The waste lead slag was used in mortar tests to evaluate it for use as a concrete aggregate. The slag's effect on the mixes was evaluated by observing the following:

Flow (workability)

Setting characteristics

Compressive strength

Unit Weight

First, a theoretical mortar mix was developed using Granthan's curves[1] as a guide. From the waste lead slag mechanical gradation curves in Chapter II, Figure 5, the average experimental gradation with a fineness modulus of 3.73 was taken along with the maximum slag size and used in Granthan's Figure 5 to obtain a 1:2.75 cement-to-aggregate ratio by volume. This ratio of 1:2.75 was then used in Granthan's Figure 8 to obtain the water-to-cement ratio of 4.5 gallons of water per sack of cement required to make a maximum density mortar. A test mix using Ciment Fondu and slag was prepared using these values taken from Granthan's curves.

Additional mortar test mixes were made based on ASTM C-87 requirements as modified in Appendix A. For these mixes two water-to-cement ratios, 4.5 and 6.8 gallons per sack, were used. After mixing the cement and water together, slag was added until a flow index of 100 ± 5 was

reached. The two W/C ratios were chosen to provide a range of test results so that a better interpretation of the slag's adaptability to concrete work could be made. More specific data on the various mortar mixes prepared are shown in Table VI.

The slag material from Herculaneum was graded by using mechanized laboratory sieve equipment with No. 4, 10, 20, and 40 size sieves installed. Material passing these sieves was remixed in the proper percentage to obtain a gradation corresponding to the average gradation shown in Figure 5. Periodic gradation checks showed that the blend remained very close to the average gradation required.

Flow (Workability)

The theoretical mix, SF2, exhibited no flow at all which indicated that Granthan's curves should not be used indiscriminately, and that mix adjustment would be required to develop the proper workability. Research work similar to that of Mr. Granthan should be carried out using sharp-shaped materials like magnetite, limonite, or waste lead slag.

The other mixes were prepared to have flow indexes of 100 ± 5 by limiting the amount of slag added to the water-cement paste. All mixes, SF3, SP1-2-4-5-6-7, and OF1, exhibited good workability although the amount of water bleeding varied. The sharp-shaped slag tends to bridge from particle to particle thereby making it easier for the mixing water to seep out. Bleeding decreased as the W/C ratio decreased.

It was interesting to note that the Ottawa Sand-Ciment Fondu mix, OF1, had the highest cement-to-slag ratio at a flow index of 100. The

TABLE VI

MORTAR MIXES

(Per ASTM 87-58T)

Mix No.	2" Dia. by 4" Cylinders	2" Cubes	Water/Cement Ratio Gal./Sack[a]	Constituents of Mix (Grams)						Cement/Slag Ratio By Abs. Vol.	Remarks
				H_2O	Ciment Fondu[b]	Portland Type I	Portland Type III	Waste Lead Slag[c]	$CaCl_2$[d]		
SF2	9		4.5	600	1,500			4,890		1:2.75	1. Some Bleeding 2. No Flow - Stiff
SF3	9		6.8	900	1,500			5,973		1:3.35	1. Excessive Bleeding 2. 100 Flow
OF1		9	6.8	900	1,500			4,520 (Ottawa Sand)		1:3.56	1. Slight Bleeding 2. 100 Flow
SP1	6		6.8	600		1,000		3,737		1:3.10	1. Slight Bleeding 2. 100 Flow
SP2	12		6.8	900			1,500	5,174		1:2.90	1. Slight Bleeding 2. 100 Flow
SP4	12		6.8	900		1,500		5,897	30	1:3.30	1. 105 Flow
SP5	3		4.5	200		500		1,088	10	1:1.81	1. Very Smooth Mix, 100 Flow 2. Shrinkage Observed
SP6	8		4.5	600			1,500	2,600	30	1:1.43	1. 100 Flow 2. Shrinkage Observed
SP7	8		4.5	600		1,500		2,488		1:1.37	1. 100 Flow 2. Shrinkage Observed

a. Multiply by .0889 to obtain W/C ratio by wt. Multiply by .284 to obtain W/C ratio by abs. vol.

b. Sp.gr. of Ciment Fondu 3.20.

c. Sp.gr. of slag 3.80, Ottawa sand 2.70.

d. $CaCl_2$ equals 2 per cent of cement used.

angle of repose of the material evidently accounts for this since round-shaped particles require less paste for flow lubrication than is required by sharp-shaped particles.

Compressive Strength

Figures 6 and 7 show the compressive strength versus curing time for mixes using water-to-cement ratios of 4.5 and 6.8 gallons of water per sack of cement. Three samples of each mix were broken at the end of each curing period except for SP5 which was limited to three individual breaks to obtain a trend for mixes containing 2 per cent calcium chloride ($CaCl_2$).

Only two slag-Ciment Fondu mixes, SF2 and SF3, were required to demonstrate that a high strength mortar could be obtained. The Ottawa Sand-Ciment Fondu, OF1, test specimens were made to provide a standard to compare the effect the slag might have on the mortar strength. Since the OF1 specimens were two-inch cubes, their compression test results must be reduced 33 per cent for proper comparison with the two-inch diameter by four-inch long cylinders used for mix SF3. The slag did reduce the mortar strength although not significantly.

The slag-portland Type I mixes, SP1 and SP7, produced mortar strengths above 3,000 pounds per square inch but only after several days of curing time had passed. In an effort to speed up the attainment of strong mortar, slag-portland Type III mix, SP2, was prepared and tested--without success.

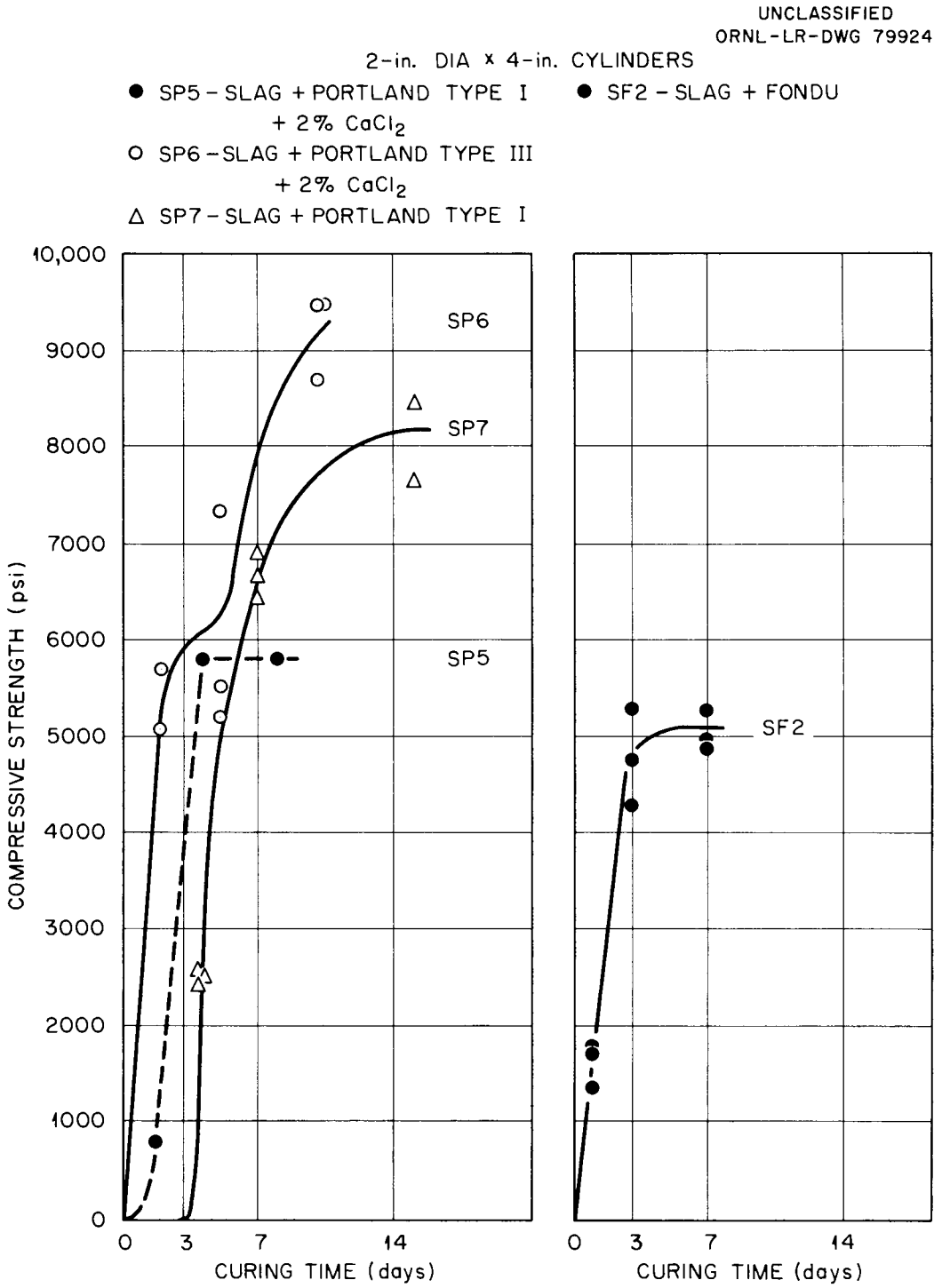


Figure 6. Compressive strength versus curing time for mixes using W/C ratio of 4.5 gal/sack, flow index 100 ± 5.

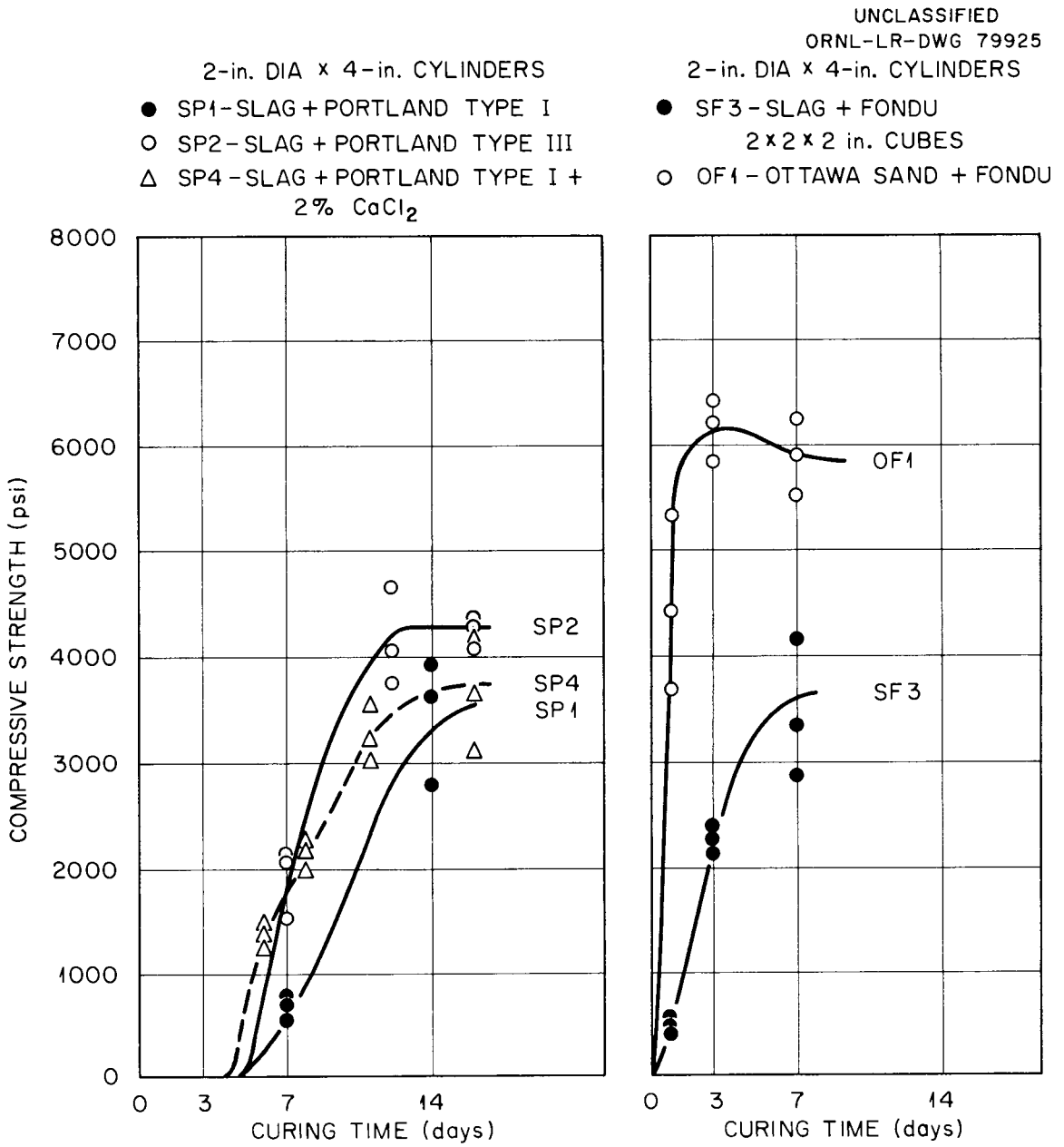


Figure 7. Compressive strength versus curing time for mixes using W/C ratio of 6.8 gal/sack, flow index 100 ± 5.

Ciment Fondu produces internal heat faster than portland cement during the hydration (curing) process. To determine if a higher internal curing temperature would hasten the attainment of a strong mortar, calcium chloride was added to slag-portland Type I and Type III mixes to provide a heat source. These mixes were prepared and tested with apparent success. Specimens of mix SP6 exhibited more than sufficient strength at two days curing time even though the retarding effect was still observable between the second and fifth curing days. This apparent success, however, was found to be limited as explained later in this report under "Setting Conditions."

Figure 8 was prepared to show the range of compression strengths obtained as the water-to-Ciment Fondu ratio went from 4.5 to 6.8 gallons of water per sack of cement. An insufficient number of tests were made to show conclusively that mixes using 5.0, 5.5, or 6.0 gallons per sack would produce strengths that would fall within the range shown. However, a curve taken from Reference 12 for Ciment Fondu concretes made with river aggregates shows the same form as the experimental results plotted in Figure 8. The strength spread of the experimental tests is a typical characteristic of concretes made with Ciment Fondu[12].

Setting Characteristics

The Ottawa Sand-Fondu mix, OF1, was also used as a standard to compare the effect the slag would have on the mortar setting time. Both OF1 and SF3 were mixed with equal water-to-Ciment Fondu ratios of 6.8 gallons of water per sack of cement. The slag did affect the setting rate as shown by the strength obtained at one day curing, Figure 7. The

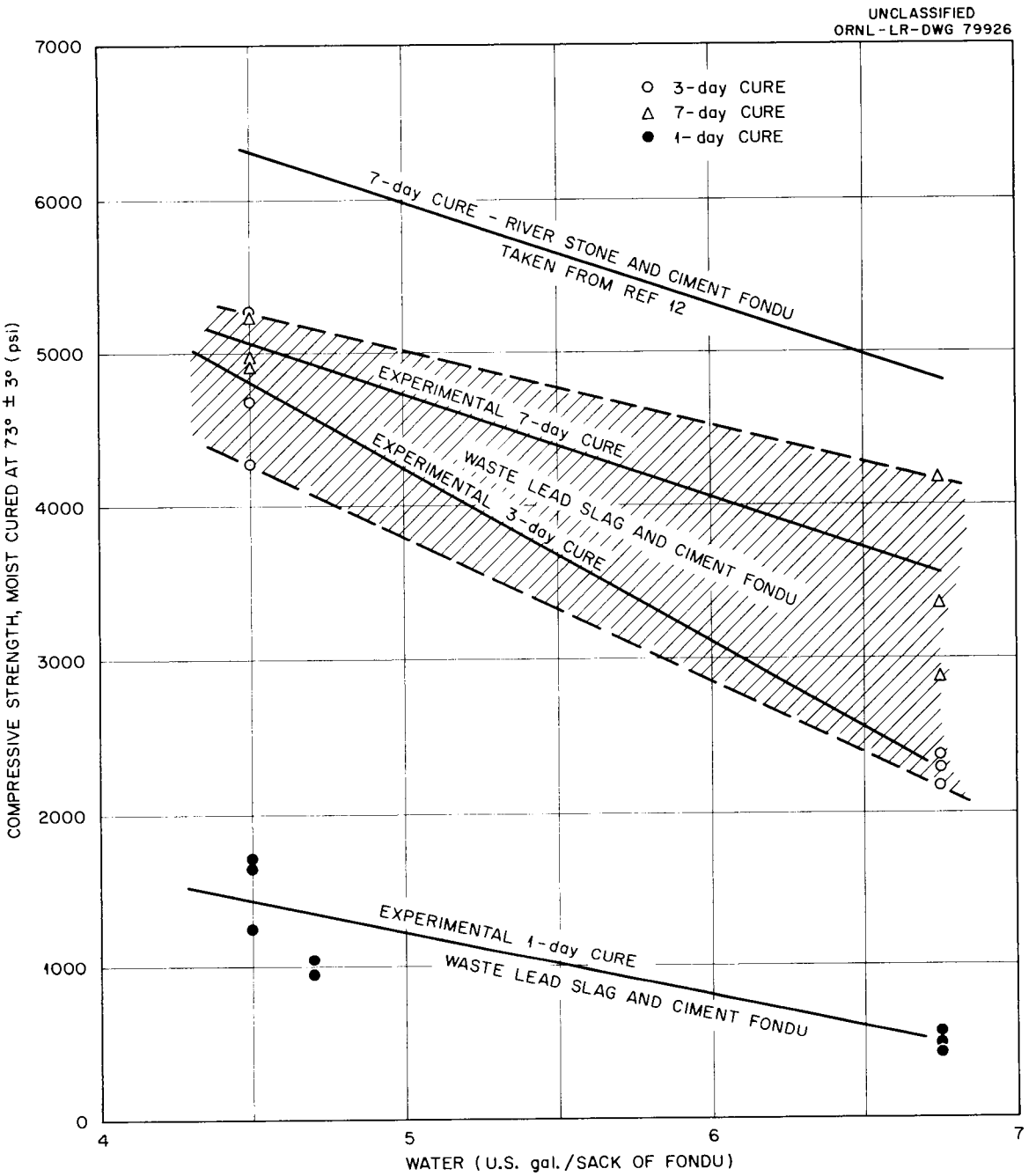


Figure 8. Compressive strength versus water/Ciment Fondu ratio.

initial set for the mixes using slag and portland cement, SP1 and SP2, was delayed by four or five days. Such a delay would not be practical for normal concrete construction work since mix water would be lost by bleeding, and since an uncertainty about the concrete quality would persist after setting did start.

Even though most of the slag plus portland mixes did not start setting up until the fourth or fifth day, their final strengths were comparable to the slag plus Ciment Fondu mixes. Chemical reasons were sought to explain this delayed-action setting characteristic.

Chemical activity caused by aggregates containing minerals or other substances that are soluble in water was investigated first. Chemically, the aluminum/calcium ratio is the only major difference between the Ciment Fondu and portland mortars (see Tables II and V). A chemical review of the typical slag analysis, Table II, showed that sulfur was the only element present which might cause trouble by forming sulfuric acid (H_2SO_4). Since only traces of sulfur are present in the slag, it was doubtful that sufficient acid could be formed to be harmful. Iron sulfide, FeS_2 (Pyrite), another material capable of forming sulfuric acid, was not indicated. In addition, Ciment Fondu is very rapidly deteriorated by exposure to sulfate attack and this condition was not observed. The insoluble sulfides present in the slag (2.0 to 3.0 per cent) should not be detrimental. There is no indication that sulfurous acid (H_2SO_3) is present. Since sulfurous acid does not exist in the free state, the only indication of its presence would come from the salts

formed. If the calcium and magnesium, present in the oxide state, formed sulfite salts, then these salts would react with the hydrated aluminates of the cements causing expansion and failure of the cement bonds.[14] Notice that this expansion would affect the hardened concrete rather than the wet mix since the salt growth is a slow process. A clue to the direct cause of the delayed-action setting was found in an abstract of a Japanese report.[18] The report, which was not available for translation, contained information on the effect lead and zinc oxide had on the set of portland concrete. Both oxides are present in the slag. It is possible that the Ciment Fondu mortar mixes were not affected by the lead and zinc oxides because of the greater amount of aluminum and smaller amount of calcium in the cement (Table V). However, experiments were not performed to verify that the aluminum-calcium ratio of the two cements controlled the setting time of the mortar mixes.

If the chemicals in the slag do delay the initial set of the mortar, the percentage of slag used in each mix should have a direct relationship to the mortar setting time. Figure 9, Compressive Strength Versus Cement-to-Slag Volume Ratio, was prepared to show that an increase in the quantity of slag used was accompanied by a strength-setting time change even though the water-to-cement ratio was held constant. The mortar mixes using portland cements, or portland cements and calcium chloride accelerator, required additional setting time as the slag content increased. The mixes using Ciment Fondu showed little effect from increased slag content which, again, could be attributed to the

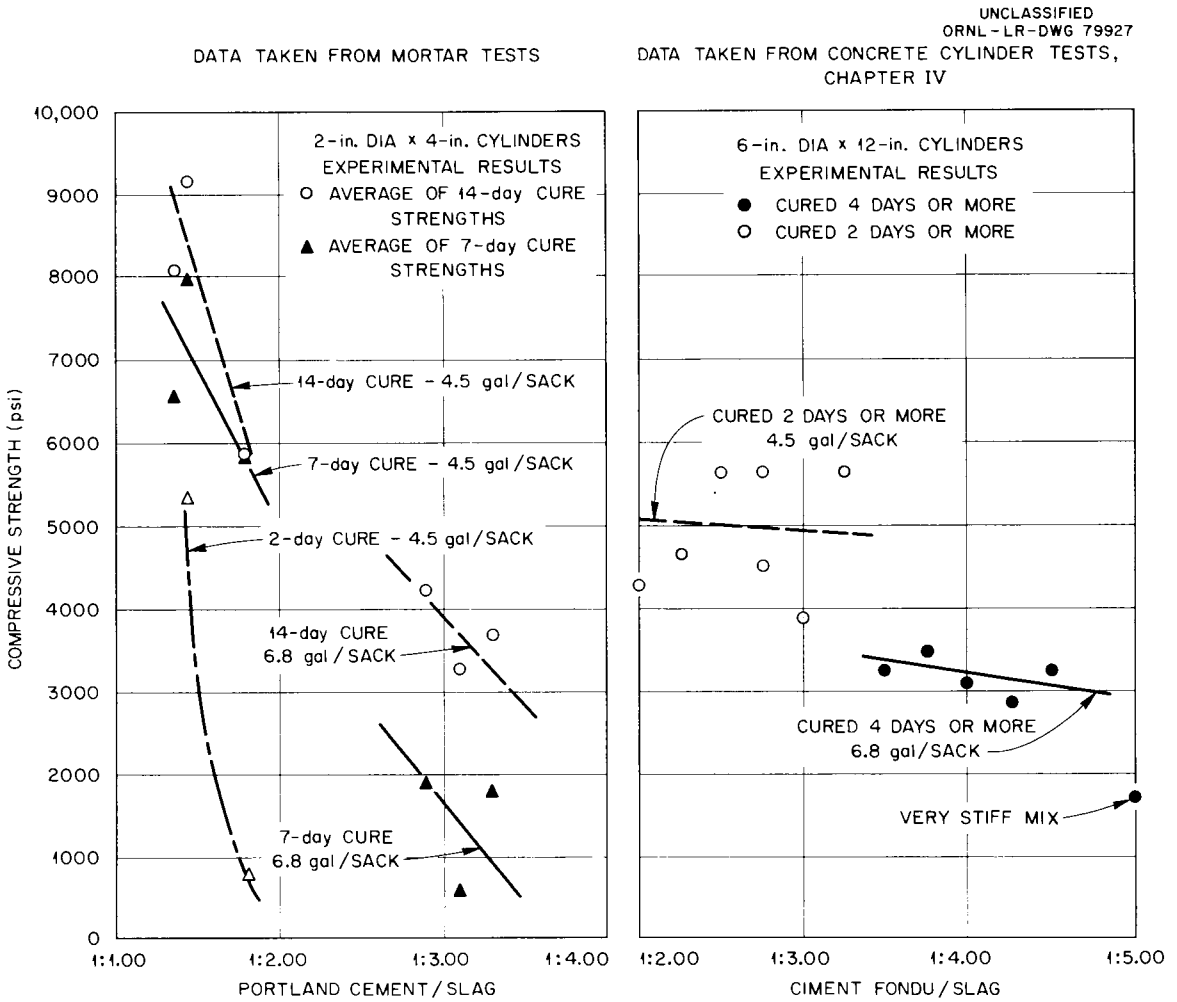


Figure 9. Compressive strength versus cement-to-slag volume ratio.

cement's aluminum-to-calcium ratio being higher than that of portland cement.

The strengths of the portland specimens are governed mainly by the amount of slag used in the mix. A portland cement-to-slag ratio less than 1:2.00 would not be suitable for making waste slag concrete due to the setting time. A portland cement-to-slag ratio greater than 1:2.00 tends to produce a waste slag concrete with too much paste although such concretes could be used if well controlled curing methods were employed and if shrinkage was not objectionable. Specimens SP5 and SP7 exhibited curing shrinkage that would be objectionable in shielding concrete.

Unit Weight

The mortar specimen unit weight ranged between 165.0 and 188.0 pounds per cubic foot. No attempt was made to obtain a maximum density mortar, but by observing the density trends of the various specimens certain conclusions were made:

A rough plot of unit weight versus cement-to-slag ratio showed that the mortar unit weight increased as the slag content increased.

Higher densities were obtained with the slag-Ciment Fondu mixes than with the slag-portland mixes. The specific gravity of the Ciment Fondu (3.20 to 3.25) accounts for some of the extra weight obtained. Density increases of less than 1 per cent were observed during moist curing periods.

CHAPTER IV

CONCRETE TESTS

The mortar test results described in Chapter III showed that strong concrete could be made with waste lead slag and Ciment Fondu. The mortar tests did not, however, provide information on the optimum density one could obtain while maintaining satisfactory workability. Several other physical properties of the concrete could not be adequately measured with the small cylinder specimens. To obtain information that would be of use in the design of waste slag concrete shielding, large compression test specimens, six-inch diameter by twelve inches long, were prepared in accordance with ASTM C-192-59 as modified by Appendix A. Twenty different mixes were prepared and subsequently tested to provide experimental data on:

Optimum unit weight versus workability

Design mix

Compression strengths

Modulus of elasticity

The following mathematical expression was written to obtain the absolute volume of each material theoretically required to produce a concrete mix.

$$C + W + S = V_t \qquad 1.$$

Where

C = absolute volume of cement

W = absolute volume of water

S = absolute volume of slag

V_t = total absolute volume of mix void of air

$$\text{Absolute volume} = \frac{\text{weight of material}}{(\text{specific gravity})\ (62.4)}$$

The applicability of this equation is limited by the workability of the resulting mix. In order to provide some reasonable limits, equation 1 was rewritten as follows:

$$C + W\ (C/C) + S\ (C/C) = V_t$$

or for mix of one unit volume

$$C + C\ (W/C) + C\ (S/C) = 1 \qquad 2.$$

Where

W/C = water/cement ratio by volume

S/C = slag/cement ratio by volume

The mortar test results of Chapter III indicated that water-to-cement ratios of 4.5 to 6.8 gallons per sack (1.3 to 1.9 by absolute volume) would be suitable as one set of limits for equation 2. The slag-to-cement absolute volume ratios used in the mortar tests would also provide a second set of limits on equation 2.

First, a water-to-cement ratio of 4.5 gallons per sack was used as a lower limit while various cement-to-slag ratios between 1:2.00 and

1:4.00 were used in equation 2 to compute several test mixes. Then, a water-to-cement ratio of 6.8 gallons per sack was used as an upper limit while various cement-to-slag ratios between 1:2.00 and 1:4.00 were used in equation 2 to compute additional test mixes.

Using the computed mix quantities, test cylinders were prepared in order to measure slump (ASTM C-143-58), wet unit weight (ASTM C-138-44), cured unit weight (by water displacement), compression strength (ASTM C-192-59), and chord modulus of elasticity (ASTM C-469-61T). Specific mix data for these specimens, SF4 through SF19 and SF100, are shown in Table VII.

Optimum Unit Weight Versus Workability

The unit weight versus cement-to-slag ratio curves for specimens SF4 through SF13 are shown in Figure 10 for comparison with the theoretical curves calculated using equation number 2. The large differences between the wet and cured unit weights for the 4.5 gallon per sack mixes were attributed to the ASTM prescribed methods used in filling the specimen molds. The ASTM C-192-59 procedure for rodding the mix at three levels as the molds were filled was followed with the mix piled above the top of the mold while the third rodding was performed. The over-filling of the molds forced cement and water paste out of the mold, especially on the high slump mixes thereby changing the cement-to-slag ratio of the concrete in the mold. The weight of the mix in the mold was also increased by displacement of the lighter cement and water with slag material.

TABLE VII

WASTE LEAD SLAG CONCRETE MIXES

Mix	Cylinders	Constituents of Mix (lbs.) H_2O c.	Fondu a.	Slag b.	W/C Gal/Sack	Slump (in.)	Wet Wt. #/cu.ft.	Wt. By Abs. Vol. #/cu.ft.	Cured Wt. #/cu.ft.	Cement/Slag By Abs. Vol.	Observations
SF4	3	11.0	25.0	8.14	4.96	-	179.5	181.2	-	1:2.75	Excessive bleeding--slump not taken.
SF5	1	4.79	11.65	22.70	4.5	>10	174.7	176.2	182.5	1:2.00	Bleeding--no stiffness at all.
SF6	1	4.94	9.45	33.75	4.5	3/8	184.8	188.5	187.2	1:3.00	Stiff--no bleeding--not enough paste to fill holes. Harsh.
SF7	1	5.17	8.46	30.10	6.7	>10	179.4	174.5	188.5	1:3.00	Soup--excessive tamping was used.
SF8	1	3.93	6.30	37.70	6.7	None	179.6	191.5	178.2	1:5.00	Stiff--harsh surface--voids (lots of them)--little curing shrinkage.
SF9	1	4.46	7.22	34.40	6.7	4 1/4	185.0	183.5	185.0	1:4.00	Not too smooth--slightly coarse--fell apart at 4 1/4" slump. Little curing shrinkage--packed into cylinder well.
SF10	1	4.32	10.44	31.00	4.5	6 1/2	180.0	182.5	183.9	1:2.50	Quite smooth--worked quite easily--some bleeding.
SF11	1	4.12	9.92	32.42	4.5	1	183.0	185.1	185.7	1:2.75	Smooth--worked a little stiff--small amount of bleeding--lots of surface voids--some smooth spots.
SF12	1	4.63	7.50	33.60	6.7	*5 1/2	183.2	181.5	186.0	1:3.75	Good workability--some bleeding--W/C slurry pushed to top during rodding. Small voids--large voids.
SF13	1	4.32	6.96	35.20	6.7	*4	180.2	185.3	182.1	1:4.25	Stiff although some paste worked to top. Slide-type slump.
SF14	1	4.35	11.02	29.41	4.5	7	175.8	179.5	182.5	1:2.25	Good mix--not too much bleeding. Good slump--cohesive.

TABLE VII (continued)

Mix	Cylinders	Constituents of Mix (lbs.) H_2O c.	Fondu a.	Slag b.	W/C Gal/Sack	Slump (in.)	Wet Wt. #/cu.ft.	Wt. By Abs. Vol. #/cu.ft.	Cured Wt. #/cu.ft.	Cement/Slag By Abs. Vol.	Observations
SF15	1	4.12	9.92	32.42	4.5	2	180.5	185.1	186.0	1:2.75	Smooth mix--little stiff to work (move)--cohesive--good slump.
SF16	1	3.77	9.03	34.85	4.5	1/8	183.1	190.0	185.2	1:3.25	Stiff--not workable.
SF17	1	4.80	7.79	32.45	6.7	7	175.9	179.5	185.6	1:3.50	Non-cohesive--sloppy-bleeding.
SF18	1	4.46	7.22	34.40	6.7	1 1/2	178.0	183.5	184.0	1:4.00	Fair cohesion--lots of water & paste bleeding--lots of surface voids--slag not covered.
SF19	1	4.18	6.74	36.00	6.7	1/4	178.1	187.0	186.2	1:4.50	Just barely cohesive--some water & paste on top.
SF100	9	34.3	68.7	265.0	5.5	2 3/4	184.0	183.5	184.0	1:3.25	Smooth mix.
SP10	1	4.46	8.06[d]	33.5	6.0	3	174.0	183.2	178.5	1:3.50	+ 2% $CaCl_2$ (73.3 gms) portland Type III. Looked like lots of air bubbles in mix. Smooth mix.
SP11	1	3.96 .16	9.76[d]	32.42	4.5	3 1/2	177.0	185.1	178.0	1:2.75	+ 2% $CaCl_2$ (88.7 gms) portland Type III.

* Slide type slump should not be used.

a. Sp.gr. of Ciment Fondu 3.20.

b. Sp.gr. of slag 3.80.

c. Total water including absorbed water of slag.

d. Portland Type III plus 2% $CaCl_2$.

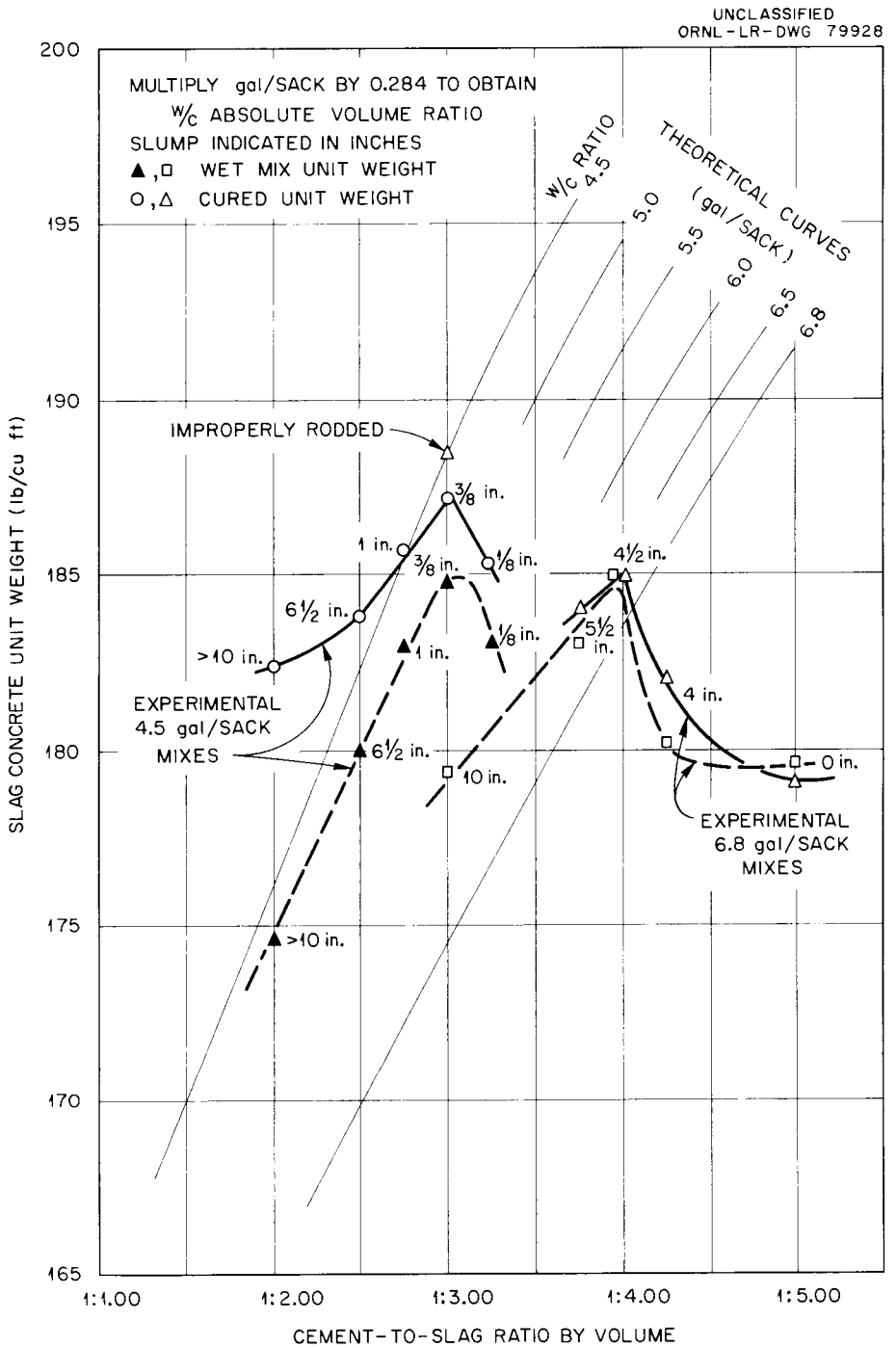


Figure 10. Slag concrete unit weight versus Ciment Fondu/slag ratio as related to water/Ciment Fondu ratio (mixed in accordance with ASTM C-192-59).

The wet and cured unit weight of the 6.8 gallon per sack mixes were quite close except for one improperly mixed specimen. Because of their high water content, these mixes exhibited excessive water bleeding during the wet unit weight testing operations, and during the filling of the molds. The bleeding water was clear indicating that little cement was lost and that the cement-to-slag ratio was not changed. The lost water changed the water-to-cement ratio and this accounted for the plotted experimental curve falling on a lower theoretical water-to-cement ratio curve (6.0 to 6.5).

The concrete unit weight was observed to decrease as the mixes became too stiff to exhibit workability. Sufficient quantities of water and cement were not available to fill the void spaces in the mix. These unfilled void spaces were also noted at the time the specimens were broken for strength values.

The plotted experimental values of Figure 10 could not be adjusted to reflect the cement-to-slag ratio changes caused by the mold filling operations. Six subsequent tests indicated that other factors might be responsible for the differences between wet and cured unit weights.

Six specimens, SF14 through SF19, were made in an attempt to correct the errors experienced during the first tests. The mold filling operation was modified to prevent loss of cement-water paste. The molds were filled in the ASTM prescribed manner except that the over-filling was omitted to prevent the loss of any material. The 0.1 cubic foot container used to measure wet unit weights was also not over-filled. The

resulting experimental wet and cured weight values showed a greater difference than that obtained from the first tests although the modified filling procedure did produce a more uniform spread between the experimental curves, as shown in Figure 11. Since the curves are more uniformly spaced, it is reasoned that density changes following the wet unit weight measurements accounted for the differences between wet and cured values. A basis for such reasoning was found by closely observing the mix during mixing operations, and the test specimens during their curing period.

The wet mixes exhibited many small bubbles similar to froth. This froth was not visible very long after mixing operations were stopped, but such foaming would tend to increase the mix volume if the bubbles were trapped within the mix. Air content of the wet mix varied from 0 to 9 per cent. The specimen molds were twice as tall as the six-inch high container used to make wet unit weight measurements. This additional static head and rodding operations either compressed or displaced some of the trapped air bubbles to provide more solid material per unit volume. Therefore, the wet unit weight of the concrete in the mold was greater than the wet unit weight in the 0.1 cubic foot container.

The unequal height of the mold and container did not seem to be able to account for all of the density differences. Additional differences occurred during the curing period. The weight of the wet concrete in the molds was recorded and compared with the weight of the cured cylinder at one day. An average of 0.26 pound of water per cylinder,

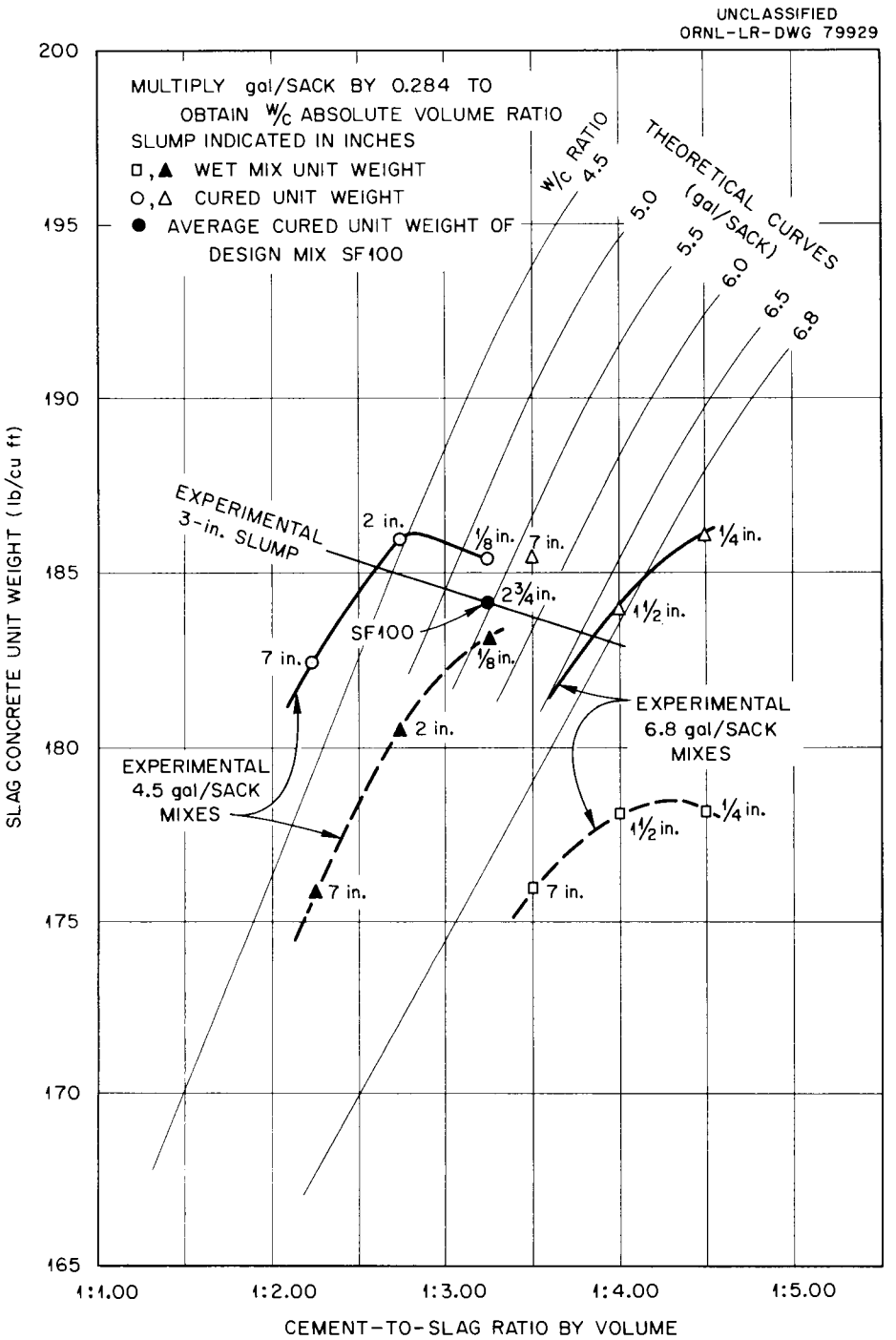


Figure 11. Slag concrete unit weight versus Ciment Fondu/slag ratio as related to water/Ciment Fondu ratio (mixed in accordance with ASTM C-192-59, modified as noted in Appendix A).

or 1.35 pounds per cubic foot, was lost by bleeding. The loss of the water, and the trapped air bubbles driven out by the high curing heat of hydration, permitted greater consolidation of the mix to take place before initial setting prohibited further movement. Air bubbles were observed in the water standing on top of the molds, and the sides of the molds became very warm during the first twelve hours of curing. Air content of the cured specimens varied from 0 to 2 per cent. If the mix did consolidate itself into the space occupied by the lost water, approximately 7.5 pounds per cubic foot would be added to the weight of the concrete. The curves of Figure 11 indicate unit weight gains from 2.5 pounds to about 8.0 pounds per cubic foot for the cured concrete.

In spite of the difference between the wet and cured unit weight values obtained, the cured values did fall within an acceptable range of the theoretical values derived by using equation number 2. To check the validity of the test results a design mix was taken from the curves of Figure 11, and from the curves of Figure 8, Chapter III.

Two specimens, SP10 and SP11, were made using waste lead slag, portland cement Type III, and 2 per cent calcium chloride to verify the conclusion reached during the mortar tests that cement-to-slag ratios greater than 1:2.00 by volume would not produce satisfactory concrete. Initial setting started during the fifth day for specimen SP10 (C/S = 1:3.5) and during the third day for specimen SP11 (C/S = 1:2.75).

Design Mix

The experience gained during the mortar tests was used to establish a desired concrete strength for the design mix. Figures 6 and 7 showed that strength of the slag-Ciment Fondu mixes leveled out by the end of a seven-day curing period. The Recommended Practice and Standard Specifications for Concrete and Reinforced Concrete, June 1940, recommends increasing the desired concrete strength by 15 per cent for design. Thus, since a concrete strength of 3,000 pounds per square inch was desired for the test cylinders, the design mix was based on a strength of 1.15 times 3,000 or 3,450 pounds per square inch. In Figure 8 the water content required for 3,450 pounds per square inch concrete was taken from the lower edge of the band as 5.5 gallons per sack of cement. Figure 11 was used to obtain the rest of the constituents of the mix for a three-inch slump concrete.

5.5 gallons/sack

1:3.25 Ciment Fondu/slag

Equation 2 was used with V_t equal to one cubic yard to obtain the following design mix (SF100):

Water	452 pounds
Ciment Fondu	928 pounds
Slag	3,580 pounds
Cement Factor	9.9 sacks
Yield	2.73 cubic feet/sack

The average cured unit weight of the nine cylinders made from the design mix is plotted on Figure 11. The fourteen-day-old specimens exhibited a weight of 184.5 pounds per cubic foot which was only 0.5 per cent above their one-day density. The workability of the design mix, as measured by a slump of 2 3/4 inches, was very close to the three-inch value expected. Actually, it was observed that good workability occurred with all of the mixes tested when they fell within the slump range of two to six inches.

Compression Strengths

The design mix cement factor is high and yield is low by normal portland concrete standards for a comparable 3,450 pounds per square inch mix. However, the cement quantities reported above for the slag-Ciment Fondu concrete are consistent with those recommended in the booklet titled Ciment Fondu for the Engineer and Contractor[16] and the letters received from the Lafarge Aluminous Cement Company, Limited[7]. In general, more Ciment Fondu than portland cement is required for a concrete being used for structural purposes. The need for more Ciment Fondu is explained by the change in the nature of the cement's hydration products. On prolonged moist curing, the metastable compounds $CaO \cdot Al_2O_3 \cdot 10H_2O$ and $2Ca \cdot Al_2O_3 \cdot 8H_2O$ produced at ordinary temperatures are converted into the cubic form $3CaO \cdot Al_2O_3 \cdot 6H_2O$.[12] This conversion is reported to be very slow and probably never occurs in dry concrete. Moisture and high temperatures greatly accelerate the conversion process with the added result of strength reductions by as much as 50 per cent.[12] It was stated

previously that the test cylinders became very warm during their curing period and since they were also moist the proper conditions were present for the conversion process to take place. Therefore, high cement factors along with the proper curing methods are required in order to produce sound, strong Ciment Fondu concretes.

The degree of conversion that occurs in a concrete is very difficult to determine since conversion depends on both temperature and moisture. Similarly, the final strength of the concrete can vary considerably depending on whether full or no conversion of the metastable compounds has occurred. Compression test results of the design mix, and of the single cylinders prepared for the density investigation, are plotted in Figure 12. These experimental test results indicate that conversion variations did occur. Although curing conditions were meant to be identical for all test cylinders, some of the cylinders were not placed in the curing room until the second day rather than the first. Some of the cylinders were broken at the end of several different curing periods; therefore, they were subjected to varying amounts of temperature and moisture. Difficulty with the curing room moisture content was also experienced in that the water spraying system stopped functioning. The curing room temperature varied more than plus or minus three degrees while the water was off.

The greatest compression strengths were obtained from the nine design mix cylinders (SF100). The reason the 5.5 gallon per sack mix produced stronger concrete than the single batch mixes using 4.5 gallons

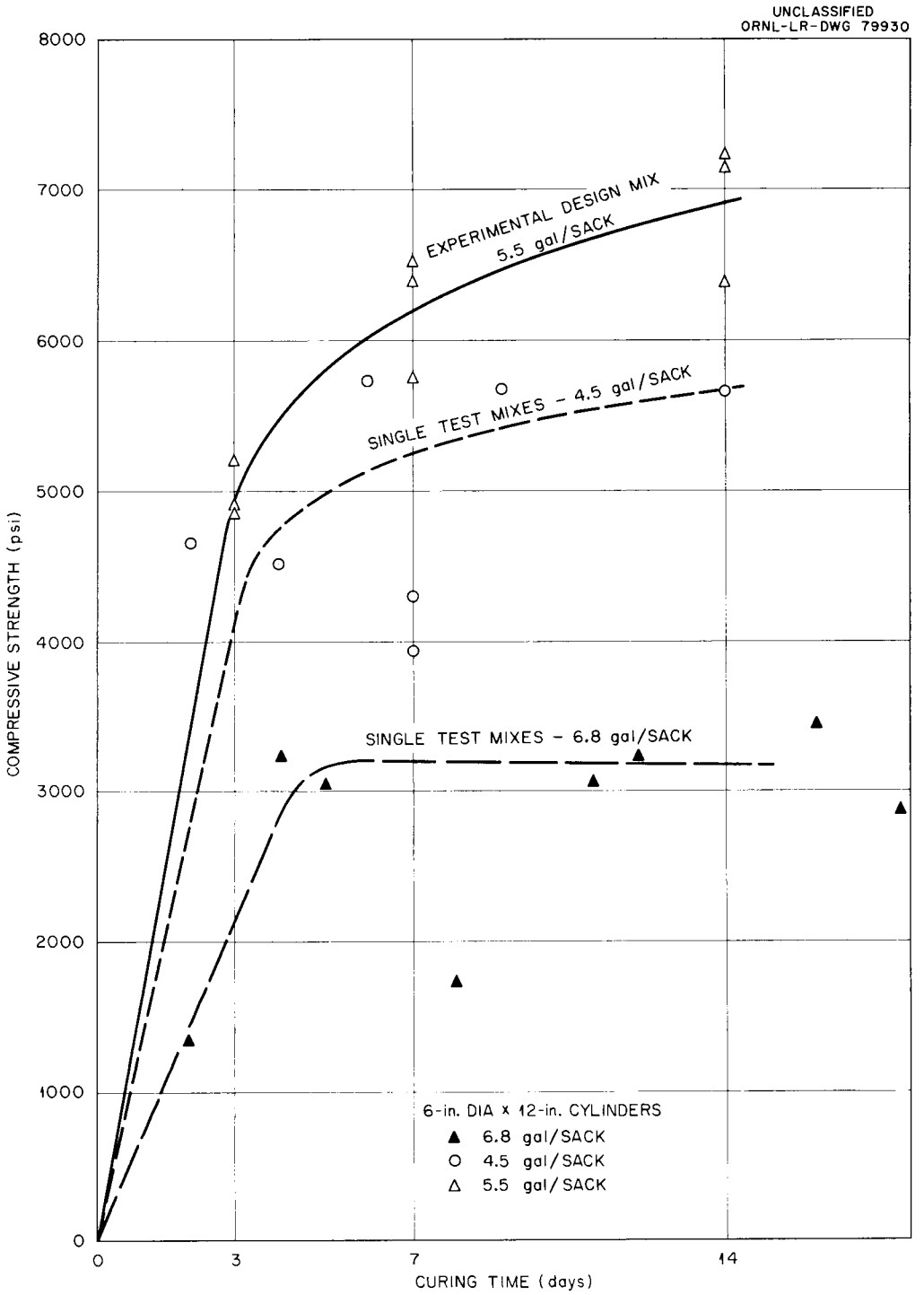


Figure 12. Compressive strength versus curing time for slag-Ciment Fondu concrete.

per sack can be partially explained by the conversion phenomenon, and by the fact that the loss of curing room humidity and temperature control occurred while these design mix specimens were curing. Cooler curing temperatures would retard and possibly eliminate the strength reducing conversion process, and this might account for some of the greater strength. The manner in which Figure 8 was established accounts for the rest since an insufficient number of specimens were tested.

The pounds per square inch compression strength of the slag-portland specimens, SP10 and SP11, was 3,180 at eleven days and 3,020 at eight days respectively. These strength results are adequate but they do not offset the time required for initial setting to take place. The interior of the specimens, observed after breakage, contained some slag that had not been bound by the mortar. The shear plane of the broken specimens contained some sheared slag and some pockets where slag had been pulled out of the mortar.

Modulus of Elasticity

Modulus of elasticity tests were performed on the three fourteen-day-old test specimens of the design mix in accordance with the procedures of ASTM C-469-61T. Chord modulus of elasticity values for the three specimens were calculated using the following equation and the curves plotted in Figure 13.

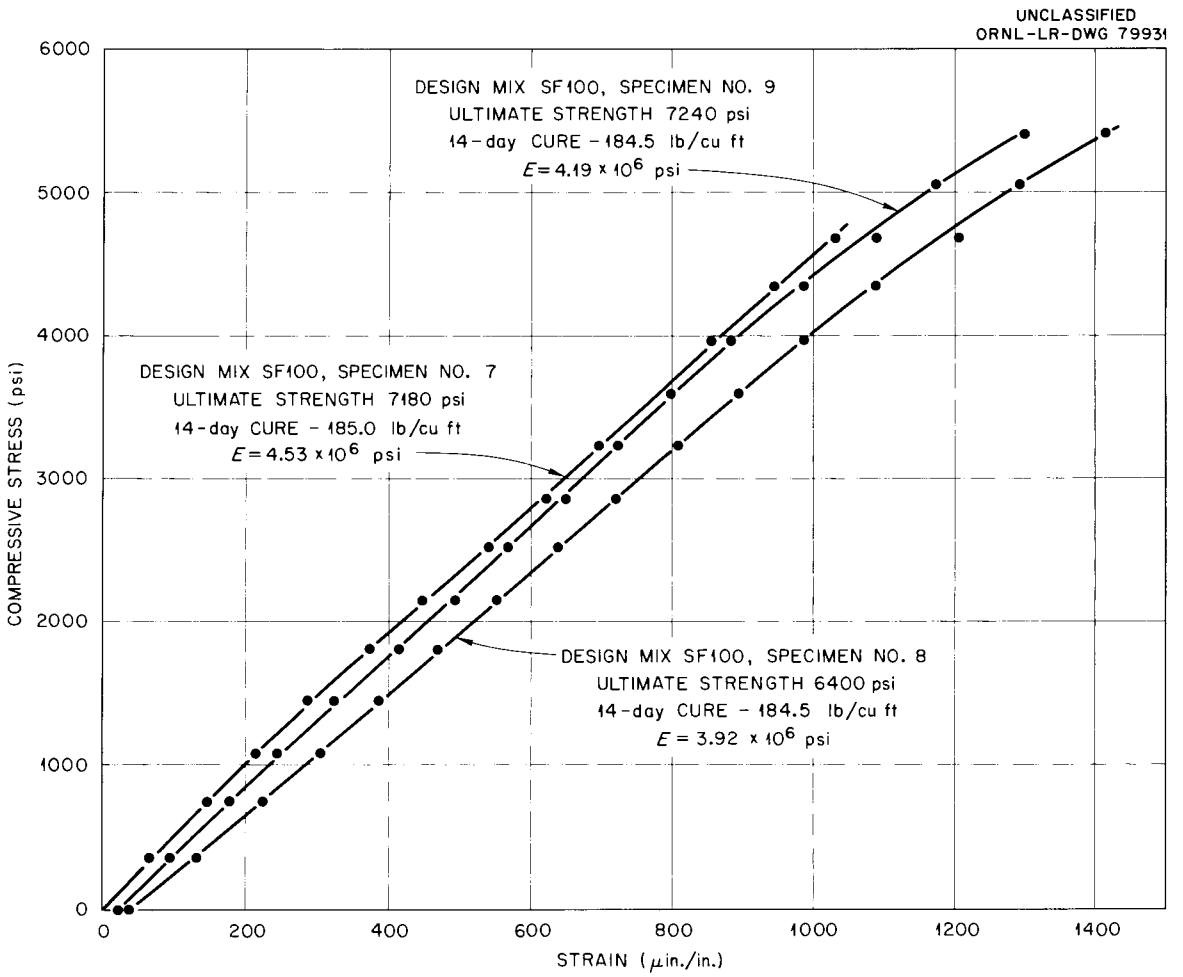


Figure 13. Compressive stress versus longitudinal strain.

$$E = \frac{S_2 - S_1}{\varepsilon_1 - 0.000050}$$

where

E = chord modulus of elasticity in pounds per square inch

S_2 = stress corresponding to maximum applied load, in pounds per square inch

S_1 = stress corresponding to a longitudinal strain of 50 microinches per inch, in pounds per square inch

ε_1 = longitudinal strain produced by stress S_2

The average value obtained for the chord modulus of elasticity was 4.21×10^6 pounds per square inch. Modulus of elasticity values for barytes concretes range from 4.00 to 4.50×10^6 pounds per square inch. Magnetite concrete modulus of elasticity values range from 4.30 to 5.49×10^6 pounds per square inch[17].

CHAPTER V

CIMENT FONDU CONCRETES

A better understanding of concretes made with Ciment Fondu, or calcium aluminate cement, was obtained through correspondence with the Lafarge Corporation's office in London, England. The available technical data on calcium aluminate concretes is very sparse when compared with the published portland concrete works. There are some basic properties of the calcium aluminate concretes which could be applied to the waste lead slag concrete in general. The most interesting properties, obtained from the correspondence, include Ciment Fondu concrete weights, water retention versus temperature, freeze-thaw characteristics, and concreting precautions.

Unit Weight

Ciment Fondu concretes exhibit three to five pounds per cubic foot higher unit weights than portland concretes made with the same mix and aggregates. This property was also evident from the results of the waste slag concrete tests which showed Ciment Fondu concretes were as much as eight pounds per cubic foot heavier than the portland cement concretes made with the same mix proportions (Table VII - SF11, SF17, SP10 and SP11).

Water Retention Versus Temperature

Figure 14 shows a graphic comparison of the water retained at various temperatures by portland cement and by Ciment Fondu. The greatest differences in retained water occur below 200 degrees centigrade.

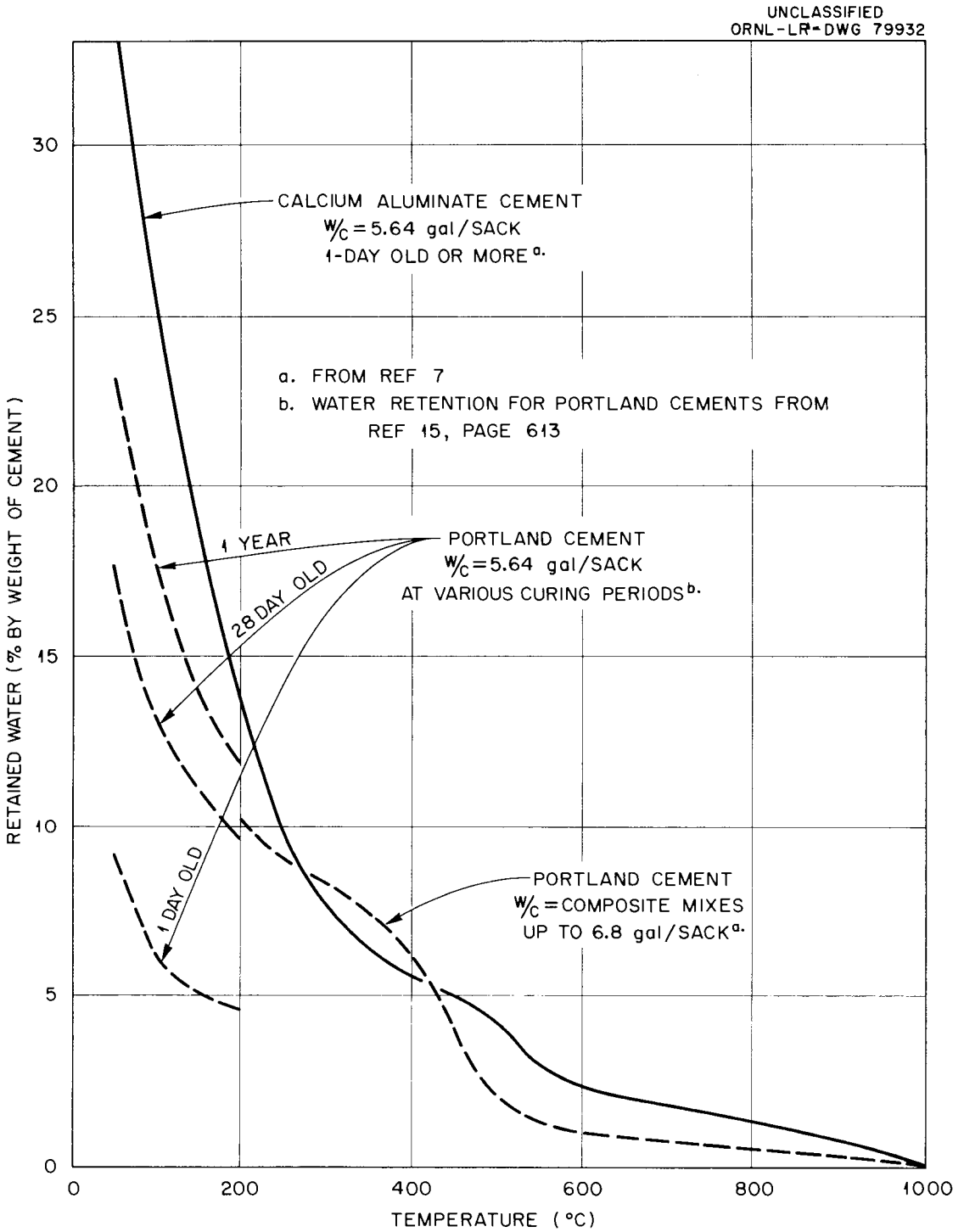


Figure 14. Water retained on heating ordinary portland cement and calcium aluminate cement at various temperatures.

The Ciment Fondu hydration process is essentially completed in twenty-four hours; therefore, the retention curve shown can be applied to any concrete older than one day. The water retention of portland cement is much more dependent on the length of curing period.

It is generally recognized that portland cement concrete should not be used above 200--300 degrees centigrade. Ciment Fondu is reported to be stable up to its melting point which is over 1,350 degrees centigrade. The expansion characteristics of aggregate materials at these high temperatures can disrupt a concrete's strength; therefore, care must be exercised in selecting proper materials. The feasibility of using waste lead slag for high temperature concrete was not investigated.

Freeze-Thaw Characteristics

Since Ciment Fondu combines with a higher proportion of the mixing water than does portland cement, the concrete has a lower porosity and permeability. Freeze-thaw resistance of calcium aluminate cement concrete has been reported to be higher than that of an equivalent portland mix.[7] Air-entrainment is not considered to be necessary.

Concreting Precautions

Ciment Fondu is handled and mixed in the same manner as portland cement. The major difference between the two cements is their chemical action. The total heat evolved during Ciment Fondu hydration is of the same order as that of portland cement but it occurs over a much shorter period of time. Special precautions are required to minimize this heating

including utilization of cold mixing water and cooled aggregates, early stripping of forms, spraying of water on set concrete or on steel forms, and limitations on concrete mass.

Shielding concrete is mass concrete. The Ciment Fondu's heat of hydration places a severe restriction on large, thick units of concrete, but the temperature rise can be controlled by limiting the depth of lifts and efficient water-curing. The depth of lift should be restricted to eighteen inches with successive lifts added every twenty-four hours. (This would not be a great restriction on pneumatically placed concrete since each lift is small.) Each lift must be water cured by sprayed water. Steel formwork may be left in position providing water is applied to the forms during the first twenty-four hours. Where massive units of concrete are essential additional cooling can be obtained by providing a system of cooling water pipes at twelve- to eighteen-inch centers throughout the concrete. The cooling water is applied to keep temperatures attained during hardening below 80 to 85 degrees Fahrenheit within the first twenty-four hours. Higher curing temperatures accelerate the conversion process, described in Chapter IV, which could reduce the concrete's strength by 50 per cent. Certain load bearing mass shielding walls could withstand considerable strength reductions yet exhibit compressive strengths above 3,000 pounds per square inch since the concrete tests demonstrated that initial strengths of 6,000 pounds per square inch were easily obtainable.

A large amount of Ciment Fondu is used for piles, reinforced concrete beams, etc., and also for plant-produced prestressed refractory floor beams. For any structural application, it is recommended that the water-cement ratio be as low as possible, and that consolidation be obtained by vibration equipment. Accelerators such as calcium chloride are unnecessary and usually deleterious.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

The test results described in previous chapters show that a strong concrete weighing approximately 185 pounds per cubic foot can be made using water, waste lead slag, and Ciment Fondu. The complete tests have also shown that concrete made using water, waste lead slag, and portland cements, or portland cements and calcium chloride, does not set rapidly enough to be suitable for normal construction work.

Although success can be claimed for producing a waste lead slag concrete, it is obvious that because of unit weight this concrete cannot be considered as a shielding material replacement for all of the present high density concretes. The waste lead slag concrete does, however, represent a shielding material that could fill the gap between 150 pounds per cubic foot normal concrete and 220 pounds per cubic foot barytes or magnetite concrete. A twenty-four-inch thick concrete shield wall would have to be increased in thickness by five inches if slag concrete was used in place of barytes or magnetite concrete. On a pound-for-pound basis, the waste lead slag concrete materials are 30 per cent cheaper than barytes and magnetite concrete materials, F.O.B. Oak Ridge, Tennessee.

The experimental slag concrete design mix turned out to be almost identical to that of the theoretical slag concrete derived for conventional placement. Therefore, the shielding coefficients originally

calculated for the theoretical slag concrete can be applied to the experimental design mix. (Mass attenuation coefficients for neutrons, Σ_r/ρ = .0356 cm^2/gm; and mass attenuation coefficients for 6 Mev gamma rays, μ/ρ = .0263 cm^2/gm). The slag concrete neutron shielding coefficient is higher than that reported for barytes and magnetite concrete values[9,11]. The high retained water characteristic of Ciment Fondu accounts for the slag concrete's greater ability to attenuate neutrons.

Massive items made of waste lead slag concrete should be adequately cured to dissipate the heat of hydration that builds up during the first ten to twenty-four hours. Water cooling of steel forms, eighteen-inch maximum lifts, and the early stripping of forms may be required to prevent loss of concrete strength from overheating. The construction season, winter or summer, will dictate the exact curing procedures needed. It is obvious that this characteristic of the slag concrete would prove to be of value in cold weather placement. Strength losses up to 50 per cent could be experienced by exercising improper curing control; yet in this case the slag concrete could still provide a compressive strength in excess of 3,000 pounds per square inch if properly designed.

The above conclusions are based on the results of the experimentation and investigation work just completed. At present, only strength, density, and cost for conventionally placed slag concrete can be reasonably judged. Various other physical properties which have not been tested for evaluation include thermal expansion, specific heat,

conductivity, water retention at high temperatures (over 200°C), density by pneumatic placement, and bond strength. All of these properties would add to the understanding of the slag concrete's usefulness.

Further experimental work could be carried out on the following specific items.

Optimum Gradation for Sharp-Shaped Aggregates

Experimental work similar to that of Mr. Granthan's work with round-shaped barytes aggregates could be carried out to provide data for mix design criteria oriented to produce optimum density concretes containing sharp-shaped aggregates.

Thermal Properties

Normal concretes are limited by the portland cement's ability to withstand heat over 200 degrees centigrade. The Ciment Fondu possesses a temperature limit well over 1,000 degrees centigrade and experiments could be carried out to determine the waste lead slag's limitations for high temperature shielding applications where density, water retention, and strength are important parameters. If the waste lead slag is to be adapted to high temperature shielding usage, thermal expansion, specific heat, conductivity, and diffusivity values would be required.

A similar project using Ciment Fondu and serpentine aggregates could be pursued.

Waste Lead Slag Concrete Made With Portland Cements

Experiments directed specifically at determining why the portland cement hydration process is retarded when waste lead slag is present could be conducted. If necessary, a special treatment of the waste lead slag would be economically feasible if it permitted portland cement to be used since Ciment Fondu represents approximately 60 per cent of the slag concrete material costs.

Waste Lead Slag Concrete Placed Pneumatically

The waste lead slag concrete unit weight of 184.5 pounds per cubic foot was obtained by conventional methods. Experiments employing pneumatic placement methods could be conducted to determine maximum concrete weight and placement costs. Using pneumatically placed magnetite concrete as a comparison, this type of project offers the distinct possibility of producing a waste lead slag concrete equivalent in weight to barytes concrete at half the material cost.

The author is hopeful that additional studies using the waste lead slag will be conducted either by other graduate students, or by interested personnel associated with the challenging field of structural radiation shielding.

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APPENDIX A

The physical property tests required by this thesis were performed as specified by the American Society for Testing and Materials[5] with exceptions as noted below. The tests included:

ASTM D 75-59 "Sampling Stone, Slag, Gravel, Sand and Stone Block for Use as Highway Materials", paragraphs 12, 13, 14 (c) -(a), and 15

Since approximately one million tons of material were available at the stock pile, the "sample per 50 tons of material" requirement was not followed. (This would have required twenty thousand samples.) Ten samples were taken on the slope of the largest waste slag pile, five at the top, one at the middle, and four at the bottom.

ASTM C-136-61T "Test for Sieve or Screen Analysis of Aggregates"

All material greater than a No. 4 sieve opening was screened from the samples prior to the start of the mechanical analysis tests.

Sample splitting method (dry) was used.

Approximately five hundred gram samples were used since more than 5 per cent of material was retained on the No. 8 sieve.

Sieving was performed mechanically.

ASTM C-127-59 "Standard Method of Test for Specific Gravity and Absorption of Coarse Aggregate"

ASTM C-128-59 "Standard Method of Test for Specific Gravity and Absorption of Fine Aggregate"

A 250-milliliter flask was used in place of a 500-milliliter flask.

Two hundred fifty gram samples were used in place of 500 gram samples.

Samples were not cooled to room temperature in a desiccator, but were weighed immediately after being removed from the drying oven.

ASTM C-117-61T "Standard Method of Test for Amount of Material Finer Than No. 200 Sieve in Aggregates"

Residue was not retained for check.

ASTM C-40-60 "Standard Method of Test for Organic Impurities in Sands for Concrete"

ASTM C-29-60 "Test for Unit Weight of Aggregate"

ASTM C-30-60 "Test for Voids in Aggregate for Concrete"

ASTM C-87-58T "Measure Mortar-Making Properties of Fine Aggregate"

Tests were made after various days of curing.

ASTM C-192-59 "Making and Curing Concrete Compression and Flexure Test Specimens in the Laboratory"

Only one cylinder per mix was made for unit weight versus cement to slag evaluation.

Six cylinders were made for compression versus curing time as governed by W/C ratio.

Filling and rodding procedure was modified to prevent the overfilling of the test molds for six mixes.

ASTM C-143-58 "Slump of Portland Cement Concrete"

ASTM C-138-44 "Weight per Cubic Foot, Yield, and Air Content (Gravimetric) of Concrete"

Wet unit weight was measured with 0.1 cubic foot container.

Filling and rodding procedure was modified to prevent the overfilling of the containers for six mixes.

ASTM C-469-61T "Static Young's Modulus of Elasticity and Poisson's Ratio in Compression of Cylindrical Concrete Specimens"

Poisson's ratio was not determined.

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