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KNOLLS ATOMIC POWER LABORATORY
Schenectady, New York

THE USE OF FERROPHOSPHORUS AGGREGATE IN MAKING HIGH-DENSITY CONCRETE

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ABSTRACT

High-density concretes for possible nuclear shielding application were made, and density and compressive strength tests were completed. Several types of aggregates were employed with emphasis on using ferrophosphorus, a by-product from phosphorus production. Densities ranging around 300 lb/ft^3 could be obtained with compressive strengths of 3000 psi or better.

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INTRODUCTION

In recent years, considerable interest has been shown in the development of high-density concrete for nuclear shielding. Examples of the practical application of this work are manifested in the type of shields which are being employed with the Brookhaven National Laboratory reactor at Long Island, New York and the Materials Testing Reactor at Arco, Idaho.

Generally, these high-density concretes require: (1) good strength and aging characteristics for structural reasons, (2) high density for effective nuclear shielding, (3) good workability to permit the use of standard concrete construction methods, and (4) low-cost material ingredients consistent with density requirements.

BACKGROUND

One of the first high-density concretes investigated was magnesium oxychloride cement mortar concrete which used small steel shot as the fine aggregate, approximately one-inch steel punchings for the course aggregate, and a mixture of magnesium chloride solution and magnesium oxide powder as the cement paste. This M-O concrete mix gives high densities (about 350 lb/ft^3) and has a high water content* (about 21 lb water/ft^3 concrete). However, it is expensive (approximately $\$400/yd^3$ for materials) and requires care in pouring and tamping to prevent aggregate segregation because of the poor size gradation. Long-range testing showed its strength decreased after six months' aging.** This decrease in strength was attributed to the fact that the steel aggregate rusted and thus weakened the bond between the aggregate and the cement. Consequently, it was felt that if the steel could be replaced by a nonrusting aggregate which has a specific gravity close to that of steel and which is available in sufficient quantities to keep costs down, then a concrete mix could be obtained that would have high density, high water content, good strength with age, and reasonable cost.

One such material that satisfies the requirements of rust resistance and availability is ferrophosphorus. This material is produced as a by-product in the production of elemental phosphorus from phosphate rock. Chemically it is a mixture of Fe_3P, Fe_2P, and FeP with a typical analysis running 70% Fe, 24.5% P, 3% Mn, 1% Si, and 1% Ti. It has an apparent specific gravity ranging from 6.3 to 6.8.

Two suppliers of ferrophosphorus are Victor Chemical Works, Chicago, Illinois and Monsanto Chemical Company, St. Louis, Missouri. The ferrophosphorus used in these tests was obtained from the Victor Chemical Works.

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*While high water contents are more desirable where neutron shielding is required, the true relationship between concrete water content and neutron attenuation has not been experimentally established as yet.

**Unpublished data from Oak Ridge National Laboratory.

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In the fall of 1950, the Engineering Division of KAPL requested that Dr. A. S. Kitzes of ORNL make some trial batches of M-O concrete using ferrophosphorus for the coarse and fine aggregrate instead of steel punchings and shot.

ORNL reported that a good workable mix could be obtained with compressive strengths of 7500 psi being reached after 28 days' aging at 77°F and 50% relative humidity. Examination of the broken specimens from the compression tests revealed that all the breaks were through the aggregate and that the bond between the cement and the ferrophosphorus was exeedingly strong. Later reports on 200-day-old specimens averaged out at 7500-psi compressive strength. The density obtained was 275 lb/ft^3 which was lower than expected. Some of this was reportedly due to the fact that the coarse aggregate shapes were large flat irregular disks, and it was felt that better densities could be obtained with aggregate of more uniform and regular shapes.

At this point, ORNL was unable to continue further studies with this material because of the pressure of other work. Consequently, the KAPL Engineering Division undertook to continue these studies to determine the age-strength characteristics and optimum aggregate size and grading to obtain maximum density. This work was subcontracted to Professor H. G. Harlow of Union College, Schenectady.

As the tests progressed, it became evident that the use of ferrophosphorus as a concrete aggregate was not limited to making M-O concrete. It appeared that high-strength, high-density concrete could be obtained using ordinary Portland cement with considerable cost savings if lower concrete water contents were acceptable. Also, blending of ferrophosphorus with other aggregates showed promise. Consequently, the original scope of the work subcontracted to Union College was extended to investigate these other applications.

TEST PROGRAM*

Scope

Tests involving strength and density measurements and observations on workability of high-density concrete mixes were carried out in this laboratory during 1952.

Heavy aggregates including ferrophosphorus, barytes, limonite, steel punchings, and dispersed iron aggregate were supplied by the Knolls Atomic Power Laboratory. In all, 27 separate mixes were made using either Portland cement or magnesium oxychloride cement. Densities and strengths were determined. The workability of the mixes was observed and tendencies for segregation were noted as shown by the behavior of the mix while wet and by an examination of sheared surfaces of the broken specimens.

*Report on heavy concrete tests at Union College Concrete Laboratory.

General Observations

Strength of Heavy Concrete Mixes

Adequate strength can be obtained using any of the aggregates or various combinations of aggregates.

Strength-Time Relationship

Portland cement mixed with heavy aggregates continued to gain strength over a period of months in the same manner as ordinary concretes.

Magnesium oxychloride mixes using ferrophosphorus aggregates continued to gain strength over a period of months. In previous tests which used iron punchings and steel shot with magnesium oxychloride cement, the rusting of the steel aggregate caused internal stresses which soon destroyed the specimens.

Corrosion of Aggregate

The ferrophosphorus aggregate appeared clean and bright even in specimens broken after six-month storage under damp conditions. This was true for both the oxychloride and for the Portland cement mixes.

Segregation

Segregation of the aggregates was not a problem in any of the mixes containing well-graded aggregates such as the ferrophosphorus, the barytes, or the limonite. Segregation was noticeable in those mixes using steel punchings mixed with lighter aggregates.

Bond Strength of the Aggregates

All of the aggregates tested appeared to bond properly with the possible exception of the steel punchings which showed a tendency to shear along a surface of the aggregates.

Range of Densities Covered

A concrete mix can be designed using one or more of these aggregates for any density in a range extending from that of ordinary concrete at 150 lb/cu ft up to 340 lb/cu ft.

Field Tests on Density

In the laboratory mixes, densities were determined while the mixtures were in the plastic state. These were compared with the densities of the cylindrical specimens after curing. In general, the agreement between the two figures was within 1 or 2% with an average of about 1% lower density in the cured specimens. This indicates that a field check on density, sufficiently accurate for all practical purposes, can be conducted by weighing known volumes of the concrete mix as the concrete is poured. These should be tamped in the same manner as standard test cylinders to approximate the same compaction received by the concrete in the forms.

Ferrophosphorus as an Aggregate

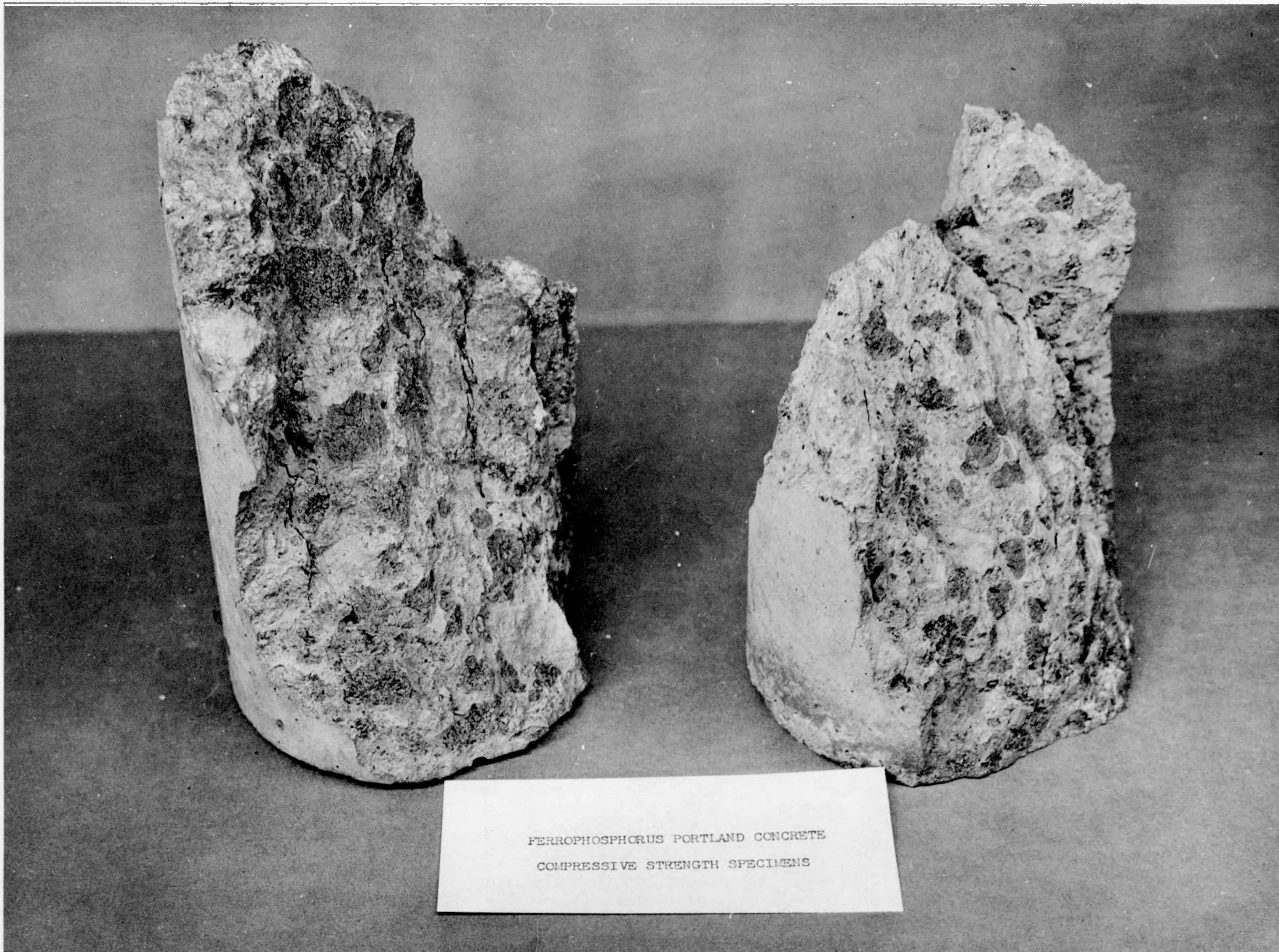
The most promising of the materials from the standpoint of workability combined with high density appears to be the ferrophosphorus. It was vastly superior in workability to any of the heavy concrete mixes which have been made in this laboratory using steel punchings, steel shot, or dispersed iron aggregate. Because of its excellent gradation and the fact that all the aggregate had the same density, there did not appear to be any tendency for the mix to segregate. The broken specimens showed a uniform dispersal of the various sizes of aggregate as shown in Figure 1120964. Mixes with either Portland cement or magnesium oxychloride consistently gave densities from 285 lb/cu ft to 300 lb/cu ft with considerable variation in proportion of coarse to fine aggregate and a good range of workability. The ferrophosphorus aggregate is somewhat friable, but strengths of the mixtures were more than would normally be required. Figure 1120965 shows samples of the coarse and fine ferrophosphorus used. The uniformity of shape was considerably better than that received for the preliminary tests at Oak Ridge.

Mixing should be possible in any conventional concrete mixer either of stationary- or transit-mix-type. Because the weight of the mixture is roughly twice that of regular concrete, the volume mixed at one time should not exceed one half the usual amount, and even smaller loads might be required. Normal mixing time should be sufficient.

No particular difficulty is anticipated in placing ferrophosphorus concrete. It behaves in much the same way as ordinary concrete. Vibrators would not be expected to produce segregation of the mix if they are used with ordinary caution. There is no reason to expect that chuting or dropping this mix for distances within the usual allowable range would cause segregation.

Dispersed Iron Aggregate

Those mixes which used Dispersed Iron Aggregate, a trade name for iron scrap ground to the size of fine aggregate, were less workable than similar mixes using fine ferrophosphorus. The D.I.A. has a high percentage of particles which are long and thin. These particles do not respond readily to tamping or vibration to produce a compact mass. They were originally intended only as surfacing materials for concrete slabs where wear and nonskid properties are important. For that purpose, they have proved to be satisfactory, but their shape does not lend itself to the production of very dense concrete.


FERROPHOSPHORUS PORTLAND CONCRETE
COMPRESSIVE STRENGTH SPECIMENS


FERROPHOSPHORUS
FINE AGGREGATE
NO. 4 TO NO. 100
FERROPHOSPHORUS
COURSE AGGREGATE
3/4" TO NO. 4

1120965

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Taconite Ore

Samples of beneficiated taconite ore were examined but were not actually used in any of the mixes. The samples consisted of irregular balls roughly 1 1/2 inches in diameter. If they could be crushed to provide a graded aggregate, then a concrete could probably be made which would have roughly the density of limonite concrete since the aggregate itself has about the same density as limonite.

Limonite Ore

The laboratory was not able to get samples of limonite ore with a sufficiently good gradation to be used in a mix by itself. By adding ferrophosphorus in the correct sizes to give a well-graded total aggregate, concrete in the range of 255 lb/cu ft to 270 lb/cu ft was made. When D.I.A. and finely ground iron called Chemical Iron were used in conjunction with the limonite, the density was approximately 230 lb/cu ft. One sample of this mix gave a four-month compressive strength of only 2050 psi, the lowest strength found in any of the mixes. An examination of the broken sample showed segregation of the light-weight and heavy-weight aggregates. This is presumably attributable partly to the fact that two different density aggregates were used and partly because of the characteristics of the D.I.A. previously noted. The limonite ferrophosphorus mixes gave high strengths and did not show signs of segregation.

Barytes Aggregates

Barytes aggregates have been used extensively in the Arco area, and no tests were considered necessary using barytes alone. In designing a mix for the 260 lb/cu ft range, barytes was used in conjunction with ferrophosphorus. The better graded of the two mixes tried produced a density of 261 lb/cu ft with a four-month strength of 5350 psi.

Mixes Using Magnesium Oxychloride Cement

In the experiments with magnesium oxychloride cement, various trials were made in which the proportions of MgO to MgCl were varied. The optimum proportions appear to be about 60% MgCl to 40% MgO by weight. In all of the mixes, the specific gravity of the MgCl solution was kept at 1.24. Various proportions of fine to coarse aggregate were also tried. The sample of greatest density was produced when 37.5% of the aggregate was in the fine range. The concrete produced in all of the ferrophosphorus magnesium oxychloride mixes was far superior in workability and appearance to previous mixtures using steel shot and punchings as aggregate. As noted elsewhere in this report, the ferrophosphorus aggregate did not react with the magnesium oxychloride cement as had been the case with the steel aggregates. For applications where the quantity of chemically bound water is important, this combination appears to have excellent possibilities.

Discussion of the Test Results

Testing Procedures

All tests were conducted with cylinders four inches in diameter by eight inches long and were cured at about 75°F and 90% relative humidity. This size of cylinder is satisfactory for density comparison but probably gives compressive strength results that are slightly low. However, most shield constructions do not require compressive strengths over 3000 psi, and all the mixes tested with the exception of one reached this value.

Water Contents

As mentioned previously, the true shielding effectiveness of water in concrete has not been experimentally established as yet. In considering the water content of concrete for shielding calculation, it should be pointed out that not all of the water added to the original mix will remain in the concrete. Work done by the Portland Cement Association* shows that the chemically bound or so-called "nonevaporable" water may be as low as one third of the total water present in cured concrete. The remaining two thirds of the water is held by absorption, adsorption, capillary action, etc. The extent to which water, both the bound and unbound, is retained is dependent on the temperature and relative humidity conditions experienced by the concrete. With Portland cement concrete, it is perhaps more conservative to assume that only one half of the original water content is retained. In the case of $MgOCl_2$ paste, the per cent of chemically bound water is much higher so that for ordinary conditions of temperature and humidity the entire original water content can be assumed to be retained.

General Comparison of Various Mixes Tested

Ferrophosphorus M-O Concrete

These mixes consisted of ferrophosphorus fine and coarse aggregate with magnesium oxychloride cement. The first mixes were patterned after the mixes made by Oak Ridge. They gave densities of 280 to 290 lb/ft^3 but appeared to be so coarse and wet that there was a tendency toward segregation. The ratio of fine and coarse aggregates was varied along with cement paste composition to find the optimum workability and density. Mix No. 7 and 13 gave the best density along with good workability. They averaged about 300 lb/ft^3 with an initial water content of 15 lb/ft^3. Increasing the coarse aggregate size from 1 to 1 1/2 inches resulted in an increase from 290 lb/ft^3 to 300 lb/ft^3. Consequently, for large pourings even greater density could be obtained if even larger coarse aggregate sizes were employed provided the loss in strength would not be too great.

Ferrophosphorus Portland Cement Concrete

Mix No. 8 was representative of this combination giving a good workable mix with a density of about 290 lb/ft^3 and a strength of 4810 psi at 60 days. By using larger aggregate as in Mix No. 11 or 18, densities of 300 to 306 lb/ft^3 could be obtained. The initial water content is 14 lb/ft^3. This combination of

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*PCA Bulletin No. 22, "Physical Properties of Hardened Portland Cement Paste," March, 1948.

TRIAL MIXES OF HEAVY CONCRETE
UNION COLLEGE CONCRETE LABORATORY 1952 PROJECT

Mix No.	Type of Fine Aggregate	Type of Coarse Aggregate	lb/cu Ft Wet	lb/cu Ft Cured	Compressive Strength, psi	Time of Testing, Months
1	Ferrophos.	1/4- to 1-in. ferrophos.	---	288	2980	4
2	Ferrophos.	1/4- to 1-in. ferrophos.	284	282	Saved	
3	Ferrophos.	1/4- to 1-in. ferrophos.	287	282	5280	6
4	Ferrophos.	1/4- to 1 1/2-in. ferrophos.	303	299	5000	3
5	Ferrophos.	1/4- to 1 1/2-in. ferrophos.	291	287	6470	6
6	Ferrophos.	1/4- to 1 1/2-in. ferrophos.	303	301	4700	3
77	Ferrophos.	1/4- to 1 1/2-in. ferrophos.	300	296	5730	6
8	Ferrophos.	1/4- to 1-in. ferrophos.	289	293	4910	2
9	Ferrophos.	1/4- to 1-in. ferrophos.	289	289	Saved	
10	Ferrophos.	1/4- to 1 1/2-in. ferrophos.	292	291	4570	4
11	Ferrophos.	1/4- to 1 1/2-in. ferrophos.	299	300	3870	4
12	Ferrophos.	1/4- to 1 1/2-in. ferrophos.	300	302	3360	2
13	Ferrophos.	1/4- to 1 1/2-in. ferrophos.	299	298	5700	5
14	Ferrophos.	1/4- to 1 1/2-in. ferrophos.	304	303	4290	2
15	Ferrophos.	1/4- to 1 1/2-in. ferrophos.	312	309	4050	2
16	D.I.A.	1/4- to 1 1/2-in. ferrophos.	296	No Cylinder taken		
17	D.I.A.	No. 4 mesh to 1 1/2-in. ferrophos.	303	298	4130	4
18	Ferrophos.	No. 4 mesh to 1 1/2-in. ferrophos.	310	306	3290	1
19	D.I.A.	0- to 1-in. limonite	232	230	4080	4
20	D.I.A. and Chem. Iron	0- to 1-in. limonite	236	232	2050	4
21	D.I.A.	Steel punchings	341	341	4180	4
22	Ferrophos.	1/4- to 1 1/2-in. ferrophos. 0- to 1-in. limonite	257	255	5620	4
23	Ferrophos.	1/4- to 1 1/2-in. ferrophos. 0- to 1-in. limonite	262	261	4250	1
24	Ferrophos.	1/4- to 1 1/2-in. ferrophos. 0- to 1-in. limonite	264	260	4660	4
25	Ferrophos.	1/4- to 1 1/2-in. ferrophos. 0- to 1-in. limonite	271	264	4400	4
26	Ferrophos. Barytes	No. 4 mesh to 1 1/2-in. ferrophos. 1/2- to 3/4-in. barytes	254	257	2990	1
27	Ferrophos. Barytes	No. 4 mesh to 1 1/2-in. ferrophos. 1/2- to 3/4-in. barytes	265	261	5350	4

Mix No.	Quantity of Cement, lb/cu yd	Quantity of Fine Aggregate lb/cu yd	Quantity of Course Aggregate, lb/cu yd	Total Wt/yd, lb	Total Quantity of Water gal/cu yd	Remarks
1	MgO 580	2630	3940	7780		Sp Gr MgCl = 1.24
	MgCl 630					
2	MgO 575	2985	3540	7620		Sample not broken
	MgCl 620					
3	MgO 575	3210	3210	7615		
	MgCl 620					
4	MgO 420	2835	4245	8080		Increased prop. MgCl sol.
	MgCl 580					
5	MgO ---	----	----	7750		55% of cement MgCl sol.
	MgCl ---					
6	MgO 330	2905	4360	8130		62% of cement MgCl sol.
	MgCl 535					
7	MgO 375	3185	3880	8000		60% of cement MgCl sol
	MgCl 560					
8	Portland 732	2720	4080	7920	46.5	
9	Portland 732	2720	4080	7920	46.5	
10	Portland 740	2690	4030	7850	46.5	
11	Portland 650	2490	4620	8100	41.0	
12	Portland 640	2150	5020	8150	41.0	
13	MgO 350	2870	4300	8050		60% MgCl
	MgCl 530					
14	MgO 335	2760	4580	8180		60% MgCl
	MgCl 505					
15	MgO 280	2680	4970	8350		60% MgCl
	MgCl 420					
16	Portland					Not a plastic mix
17	Portland 750	3080	3850	8050		
18	Portland 540	2970	4460	8260		Good plastic mix
19	Portland 670	2430	2740	6220	45.5	
20	Portland ---	----	----	6270	----	Lowest strength
21	Portland 835	3330	4620	9200	50.0	Highest density
22	Portland 710	2480	1660	6890	45.5	A little harsh
			1660			
23	Portland 745	2720	1730	7070	47.5	Good plastic mix
			1480			
24	Portland 640	2640	1890	7020	41.0	
			1510			
25	Portland 740	2800	2000	7130	47.0	
			1200			
26	Portland 660	1480	1480	6940	42.0	Heavy on 3/4 in.
		1110	1860			
27	Portland 640	1780	1780	7030	41.0	
		1070	1420			

mixes was the most promising of those tested. In fact, plans are currently under way to use a mix corresponding to Mix No. 8 for an extension of the Radioactive Materials Laboratory at KAPL; also additional amounts are to be used at the SIR site at West Milton, New York.

D.I.A. and Ferrophosphorus Portland Cement Concrete

The use of D.I.A. as fine aggregate mixed in an attempt to increase density was unsuccessful for reasons stated previously.

D.I.A. and Limonite Portland Concrete

This combination was tried to determine whether density and workability could be maintained and to take advantage of the low cost of limonite. Both density and workability decreased.

D.I.A. and Steel Punchings with Portland Cement

This mix gave the highest density, 340 lb/ft^3, of those tested but would cost the most. Strength was 4180 psi after four months, and workability was fair, but aggregate segregation might be a problem in large pourings.

Ferrophosphorus Limonite Portland Concrete

Here again, blending Limonite with the coarse aggregate is possible, but the same results could be achieved more directly by using straight barytes aggregate.

Ferrophosphorus Barytes Portland Concrete

Blending ferrophosphorus with barytes aggregate results in improving the density from 230 lb/ft^3 for straight barytes concrete to about 260 lb/ft^3 and in maintaining good workability.

Concrete Costs

Since the use of concrete for nuclear shielding may involve large quantities of materials, the relative cost per unit density of various types of concretes becomes important. The over-all costs of concrete materials will vary from site to site depending on the application labor costs and shipping costs from supplier to job site. The graph in Figure KH-9A2695 is based only on approximate cost of material after grading at the point of supply and does not include shipping, labor, and placing costs.

For purposes of comparison, the following material costs were assumed:

AGGREGATES

	Material	Source Location	Cost, $/short ton (carload lot) Graded	Ungraded
1.	Ferrophosphorus	Mont Pleasant, Tennessee	80	59
2.	D.I.A.	Buffalo, New York	120	
3.	Chemical iron	Buffalo, New York	120	
4.	Barytes	Elko, Nevada	15	10
5.	Limonite	Michigan	10	6
6.	Steel punchings	Brooklyn, New York	90	

CEMENTS

Material	Cost
Portland cement	$1.25/94-lb bag
Magnesium oxide, MgO	$0.08/lb
Magnesium chloride, $MgCl_2$, anhydrous	$0.16/lb

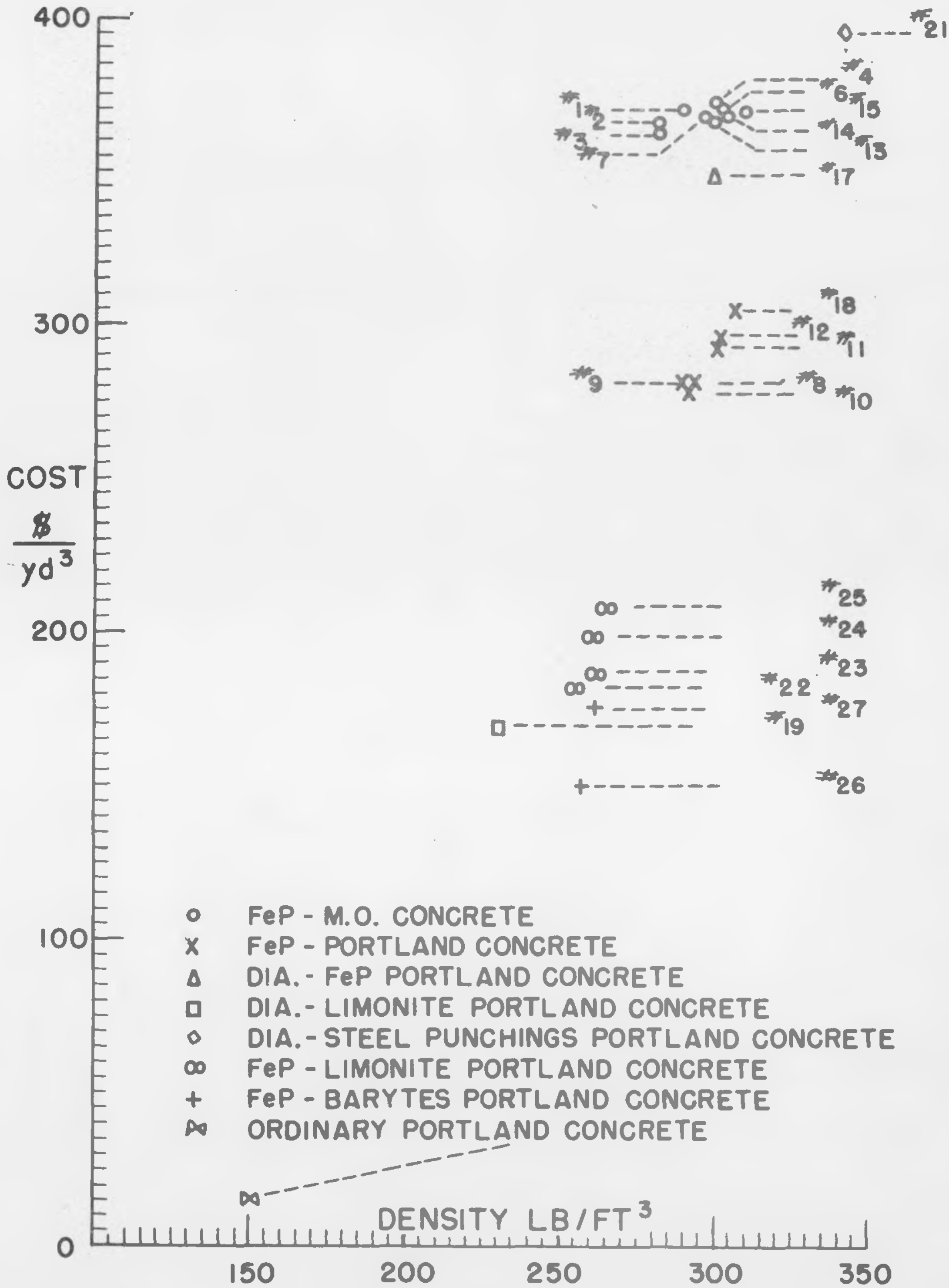
These prices are based upon cost inquiries from various vendors made during the latter part of 1952.

Figure KH-9A2695 shows the relative price grouping of the various mixes. The difference in price between the FeP - M-O concrete and the FeP Portland concrete is due to the high cost of the $MgOCl_2$ cement paste ingredients relative to that of Portland cement. It can be considered as the price differential that must be paid to obtain a concrete with a high percentage of bound water. Steel aggregates still give the highest density and further density increases should be possible if graded steel aggregate were used instead of the fairly uniform steel punchings that were employed. The extent to which cost might increase for a more closely graded aggregate would probably be the limiting factor. The FeP Portland concrete appears to be the most economical way to obtain 300 lb/ft^3 concrete.

The blending of ferrophosphorus with barytes appears interesting from the standpoint that 260 lb/ft^3 concrete can be obtained for about $150/yd^3.

GENERAL ELECTRIC CO.
KNOLLS ATOMIC POWER LAB.

CONCRETE COST vs. DENSITY



P. R. MATTHEWS MAY 2, 1953 KH-9A2695

RECOMMENDATIONS FOR FUTURE WORK

While a good workable mix of concrete can be obtained with ferrophosphorus and Portland cement, it is felt that additional work with this material is desirable. Some of the items to be studied are:

1. Lowering the cement ratio to determine whether greater densities result without too much reduction in strength or final water content.

2. Using aggregate larger than the 1 1/2-inch maximum employed for these tests to determine extent of density improvement and effects on strengths.

3. Determining additional properties such as specified heat, thermal conductivity, gas permeability, shrinkage, coefficient of expansion and radiation damage.

4. Obtaining additional age-strength data with 6-in. x 12-in. cylinders over longer curing periods.

With other concrete mixes, further work would be warranted by (1) using a more closely graded steel aggregate to obtain densities above 350 lb/ft^3 and (2) finding the optimum ferrophosphorus and barytes mixtures with respect to density and cost.

SUMMARY

Tests were made with various heavy concrete mixtures to measure densities and compressive strengths and to observe relative workability. The heavy aggregates that were used included ferrophosphorus, barytes, limonite, steel punchings, and D.I.A. The majority of the mixes included ferrophosphorus, a by-product from phosphorus production, because its use as a concrete aggregate was quite new; the primary object of the test was to determine its potentialities.

With ferrophosphorus aggregate concretes were obtained that have high density, good strength, and good workability. The mix having the highest density with the least cost consisted of ferrophosphorus fine and coarse aggregate with Portland cement. Use of ferrophosphorus fine and coarse aggregate with magnesium oxychloride cement gave a 300 lb/ft^3 concrete with a high-bound water content that showed increasing strength with age. Mixes made by blending ferrophosphorus with other heavy aggregates were tried, and the results were discussed in this report.