UTILIZATION OF WASTE ZINC SMELTER TAILINGS IN HIGHWAY CONSTRUCTION

Ву

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CHAPTER I

INTRODUCTION

General

Since the early 1920's, almost every type of imaginable material has been tried in road construction. Roads have been constructed of steel, rubber, and bricks, but all were found wanting because of high material and labor costs, extended construction time, and poor performance.

Although some of these pavements still exist, only two main types of paving operations prevail today - asphaltic and Portland cement concrete. Both of these methods of surfacing require a binder and an aggregate which constitute a large portion of total road construction expense.

Statement of the Problem

Much time and money is expended by the engineer and contractor in securing, testing, and approving aggregate for road construction.

Application of modern techniques such as aerial photography to material surveys still present the engineer with problems in locating suitable materials, and available sources are slowly being depleted. In many cases, aggregate must be transported long distances to the job site, with resulting higher construction costs.

Recent public demands for pollution control have aroused sentiment to the extent that new techniques must and will be developed to stop pollution. One of the hardest pollution problems to solve is the disposal of solid mineral wastes. However, if our economy demands that these mineral wastes be produced, then anti-pollution methods must be developed in order for man to live with them. Therefore, a common solution for the two problems might be utilization of mineral wastes as aggregate for road construction in many areas of the United States where natural aggregates are being depleted and therefore expensively transported from other regions.

Scope of This Investigation

The scope of this investigation was to determine the feasibility of using Oklahoma zinc smelter wastes as aggregate in asphaltic cement concrete, Portland cement concrete, and stabilized aggregate base course construction.

CHAPTER II

PREVIOUS USES OF ARTIFICIAL AGGREGATES

General

With rapidly growing population, the American highway engineer is confronted with building more and more roads from naturally occurring aggregates that are being both depleted and covered by expanding cities. In order to build future roads the engineer must seek materials that will be suitable and yet economically feasible.

Regardless of whether Portland cement or asphaltic cement concrete is used for road construction, the aggregate utilized must possess significant properties. These properties, determined from "standardized" tests by such organizations as the American Society for Testing Materials and the American Association of State Highway Officials, include mechanical strength, surface texture, particle shape, resistance to polishing and skid resistance, specific gravity, water absorption, chemical stability, particle size distribution, resistance to abrasion, and resistance to frost action (Ref 1).

The most economical aggregate is often the one closest to the construction site. However, even with modern techniques such as aerial photographic interpretation, nearby materials cannot always be located, thus expenses incurred by aggregate transportation increase the overall construction cost. An often overlooked method of lowering aggregate material cost is the use of synthetic or artificial aggregates, which

are generally considered to be aggregates produced by some chemical and/or physical process.

Highway engineers are always hesitant to use artificial aggregates unless they are of proven field quality. However, several types of artificial aggregates have been utilized with reasonable success under limiting conditions. The remainder of this chapter will discuss engineering properties of artificial aggregate previously used in highway construction.

Utilization of Ground Reef Shell

Extensive use has been made of ground or pulverized reef shell as an aggregate for road and airfield construction in the Gulf states region of the United States. Ground reef shell has been substituted for non-existent aggregates that would otherwise be expensive to ship from other regions. The reef shell has been used for base course construction and in the manufacture of asphaltic and Portland cement concretes (Refs 2, 3, 4).

Most shell beds are overlain with marine clays, which give the shell an appreciable amount of plasticity if good dredging operations are not employed. After dredging operations, the shell is moved to the mainland by barge where it is allowed to dry before grinding.

Base courses consisting of 100 percent reef shell as well as sand/shell mixtures with as much as 40 percent sand are used in both roads and airfields. The highest quality base course is achieved with 100 percent reef shell aggregate. Meredith reports an all shell base course is capable of withstanding airplane traffic with 50,000 lb

wheel loads and 200 psi tire inflation pressure (Ref 2). Sand/shell mixtures are best suited for subbase construction.

Hot-mix shell asphaltic concrete is manufactured with addition of coarse and fine river sands to meet gradation requirements. For a given gradation, the stability, flow, and unit weight are not sensitive to variation in asphalt content when designed by the Marshall Method. The asphalt content must be selected for the desired void properties, rather than from averaging values as done with conventional aggregates.

A problem in using reef shell arises from its maximum size and shape. Shell particles passing a given sieve size, such as the 3/4 inch, are often cup-shaped and elongated, making gradation more difficult to evaluate. Regardless of whether asphaltic or Portland cement concrete is used, Meredith (Ref 2) and Beaven (Ref 4) have indicated that a particle of crushed shell having a 3/4 inch maximum dimension is the largest size one can use in a finished pavement and obtain a level surface with desired pavement strength.

Another problem of using reef shell stems from destruction of oyster beds. Although the U.S. Army Corps of Engineers stipulate the usage of "dead reef oyster shell," commercial fishermen argue that dredging operations upset the ecology of the oyster by destroying his natural spawning grounds. Since many roads are built with state tax dollars, the engineer may have to consider public sentiment against the usage of oyster shells.

Utilization of Iron and Steel Slag

Another source of artificial aggregate is the waste product in the production of iron, called slag. As the production of iron increases

so does the quantity of available slag. Slag is available in all areas where steel mills are located but not always in a desirable condition, as will be discussed later.

There are two basic types of slag produced in the manufacture of iron. Slag called "blast furnace slag" is derived from a plant that utilizes a blast furnace; the other type is called "open hearth" or "steel furnace slag" and is produced in an electric furnace. Careful distinction must be made between the two because each has its own properties.

Blast furnace slag, the most commonly used, has been employed successfully for several decades as an "all purpose aggregate", particularly in highway construction. Blast furnace slag is utilized in subbase, base, and surface courses; in untreated form as aggregate in Portland cement and asphaltic cement concretes.

Blast furnace slag can be subdivided into three additional categories: 1) aircooled, 2) granulated, and 3) expanded or foam. Air cooled slags are produced by transferring the molten slag from the furnace to pits where it is allowed to solidify under atmospheric conditions. The bulk of slag consumption in Portland and asphaltic cement concretes is of this form.

Granulated slag is formed when the molten slag from the furnace is suddenly chilled and solidified by immersion in water. The slag expands and granulates into a "sand-like" material which possesses a natural cementing property. It is for this reason that granulated slags are generally used in subbase and base construction.

Expanded slag is formed when molten slag is treated by applying a limited quantity of water. Steam is generated on contact, thus

expanding the slag into a plastic foam. The foam, when cooled, forms a clinker that is relatively lightweight and is used in lightweight concrete.

Blast furnace slag is used quite extensively in Great Britain because of a lack of naturally occurring aggregates. Since chemical composition of slag changes as the grade of raw ore changes, the British Government has set requirements regulating the composition of this much needed aggregate. An example of these regulations is British Standard No. 1047, Blast Furnace Slag as a Concrete Aggregate, which states requirements for the ratio of lime and silica and the sulfur content (Ref 5).

The mineral constituents of blast furnace slag are very important. Calcium sulfide in blast furnace slag has been thought to cause deleterious expansion of Portland cement paste when oxidation of calcium sulfide occurs (Ref 6). However, no information on adverse effects of this type can be found in United States literature. Perhaps for this reason ASTM and Federal Specifications on blast furnace slag include no limitations on sulfide or sulfate content. On the other hand, British Standard No. 1047 limits the acid-soluble sulfate content of coarse aggregate to a maximum of 0.7 percent, expressed as SO₃, and the total sulfur content to 2 percent (Refs 5, 6).

Another rather unique property of blast-furnace slag is its relatively high water absorption, because of its porosity. Most aggregates have some small degree of absorption, and slag is one of the more absorbent types. Absorption is more apparent when used in asphaltic concrete mixtures because optimum asphalt contents tend to exceed those of conventional asphalt-aggregate mixtures. However,

British engineers have allowed for this in their British Standard Specifications by allowing the use of higher bitumen contents (Ref 5).

In the past there has been some concern regarding degregation of slag during field compaction, partially from attempts to relate the Los Angeles Abrasion Test to crushing that might take place under a roller. However, Bauman indicates that the Los Angeles Abrasion Test is not indicative of crushing which might be expected in bituminous mixes under a roller (Ref 7). Lea also agreed with this conclusion when he investigated a road test on the Great North Road in the County of Huntingdon, England (Ref 5).

Slag usage has not always given acceptable results. Crawford and Burns report excessive expansion of open hearth steel slag used as backfill material under a floor slab of a building constructed in Ontario, Canada (Ref 8). The one-story building, built on spread footings, experienced heaving of the center floor slab some three inches in the five years following construction. The chemical composition of open hearth slag is generally variable and unpredictable. Fresh open hearth slag often contains high percentages of calcium oxide or unslaked lime which will hydrate when in contact with moisture, causing large volume expansion. Crawford and Burns account for the heave of the floor from hydration of the lime and resulting expansion (Ref 8). Although the reported failure was noted in building construction, similar results could be expected in highway pavements.

Open hearth slag has been used with some success when presoaked with water to allow hydration of the calcium oxide. This often causes difficulties for the contractor with scheduling problems or need of large storage/soaking areas.

Utilization of Expanded Clay and Shale Aggregates

Use of shale aggregates, commonly not considered as suitable for highway pavements, has been developed by engineers, after a thermal treating process was developed by Stephen J. Hayde in 1917 (Ref 9). These artificial aggregates are called expanded shales, and include both expanded clay and slate aggregates.

Use of expanded shales is governed by rigid requirements. Research work at Texas A&M University has greatly increased the use of expanded shale in Texas (Ref 10). Expanded shales are currently being used in Portland cement and asphaltic concretes. They exhibit desirable features such as low weight and high strength. However, expanded shale is an aggregate which must be produced in high volume at low cost to be competitive with naturally occurring aggregates. The initial cost of establishing an expanded shale treatment plant is high, usually in the multi-million dollar bracket (Ref 9). Of equal or greater importance are the prevalent market situations and the cost of transporting the product to these markets.

Prospecting or location of the raw shales also produces problems. The material must be found in sufficient quantities to warrant the expense of a quarrying operation. During the prospecting operations undesirable materials such as weathered shale, sandstone, and limestone must be detected. Small quantities of these inferior rocks can be tolerated but should be removed during the mining or during the initial manufacturing process. The weathered shale will be weak and often break down under expansion. Sandstone will not expand and therefore increases the unit weight of the finished product. Limestone is not reactive as a normal aggregate but during the expanding process it is

converted to calcium oxide. As previously mentioned, calcium oxide will hydrate resulting in a volume increase. Small particles of calcium oxide can easily be hydrated by spraying or submerging the finished aggregate, but larger particles react more slowly and require long-term immersion in water.

Utilization of Ground Waste Glass

Another artificial aggregate currently under investigation is ground domestic waste glass. University of Missouri researchers at Rolla believe a glass mixture in asphaltic concrete will be as durable as the conventional limestone aggregates currently used. The research work currently being conducted was prompted to find a solution to solid waste disposal of refuse (Ref 11).

At this time no published information concerning results of field tests has been made. Problems can be expected with the use of ground glass as an aggregate. One important problem will undoubtedly be the public response concerning wear on their tires. Another problem that will undoubtedly receive some attention is the stripping effect between asphaltic cement and the smooth glass fragments.

Utilization of Sewage Ash

With added attention toward solid waste disposal, other artificial aggregates are being studied. This is the case with compacted sewage ash. Gray reports the properties of compacted sewage ash are suitable for its use as backfill, subbase, and building block material (Ref 12). Although the ash may not be considered a fine aggregate for subbase construction, it does exhibit desirable properties such as high strength

and rigidity. The compacted ash does not swell, slake, or lose its strength upon soaking (Ref 12). However, it is quite corrosive to metals and should be avoided when metals are to be used in accompanying construction. Sewage ash compacts as a granular material when compacted with a sheep foot roller. For this reason Gray recommends the use of a kneading type compactor be avoided to prevent excessive shear strain when compacting the ash.

Summary

The previously listed types of artificial aggregates are but a few of those in use and under investigation. Likewise, the problems and properties listed are only some of those experienced in their usage. They were listed to illustrate problems arising when artificial aggregates are contemplated for use as construction materials. Only by research and experience can one know if an artificial aggregate fulfills the accepted requirements for aggregates: Good mechanical strength, rough surface texture, cubical particle shape, good resistance to polishing, a high or low specific gravity depending upon its expected usage, moderate water absorption, chemical stability, desired particle size distribution, abrasion and frost resistance, and public acceptance.

CHAPTER III

WASTE MATERIALS TESTED

Four types of zinc smelter wastes and two sands were studied during the investigation.

Grain size distributions for each smelter waste and the two sands were determined by mechanical sieve analysis. The procedure conformed to a modification of AASHO T 27. The procedure was modified by using the data of Table 3.1 as a guide for determining the total sample weight to be sieved.

The specific gravity and percent water absorption of the four aggregates were determined by procedures conforming to modifications of AASHO T 84, T 85, and T 100 or ASTM C 127, C 128, and D 854. Modification occurred when sample weights for bulk and apparent specific gravities were determined from Table 3.2. Another modification resulted when entrapped air was removed from the samples by a vacuum system.

Two types of smelter waste were obtained from the Eagle Pitcher Company smelter located at Henryetta, Oklahoma. One of the samples from the Henryetta smelter was reddish in color and was given the name Henryetta Red Tailings, hereafter called HRT. Visual observation of individual grains revealed a very porous and cohesionless material, cubical in shape and having a sharp angular texture, as shown in Fig 3.1. The larger particles of the material were brittle in nature

TABLE 3.1
Size of Composite Samples for Sieve Analysis

Nominal Maximum Size of Particles Passing Sieve	Minimum Weight of Dry Samples, grams				
1 1/2 inch	9,000				
1 inch	3,000				
3/4 inch	2,500				
1/2 inch	1,500				
3/8 inch	1,000				
U.S. No. 4 or smaller	500				

TABLE 3.2

Size of Composite Samples for Specific Gravity Determination

Grain Size Range	Weight of Dry Samples, grams
Plus U.S. No. 4	1,500
U.S. No. 4 - U.S. No. 10	1,500
U.S. No. 10 - U.S. No. 80	1,000
Passing U.S. No. 80	1,000

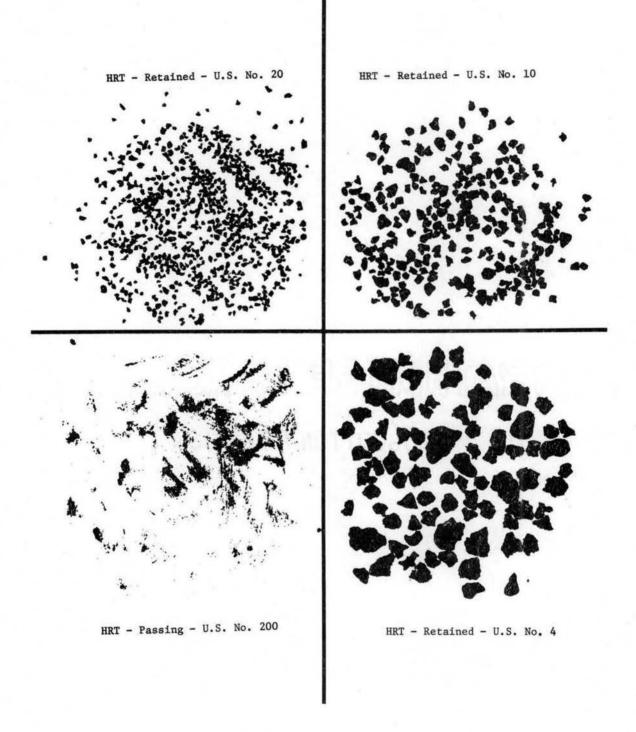


Figure 3.1. Sized Particles of Henryetta Red Tailings Illustrating Shape and Sharp Texture

but grain sizes passing a U.S. No. 10 sieve were very durable. Specific gravity, percent water absorption, and grain size distribution for HRT are given in Table 3.3.

The other cohesionless smelter waste from the Eagle Pitcher plant was similar in surface texture, particle shape, and porosity, but was black in color. This material was called Henryetta Black Tailings, hereafter referred to as HBT, and is shown in Fig 3.2. HBT also exhibited the same brittleness of larger particles and durability in smaller grain sizes as was found for HRT. Specific gravity, percent water absorption, and grain size distribution for HBT are also given in Table 3.3.

Two additional smelter wastes were obtained from the Blackwell Zinc Company located at Blackwell, Oklahoma. One cohesionless material, shown in Fig 3.3 and called Blackwell Tailings or BT in the following Chapters, was black in color. The material oxidized in the presence of water and produced a reddish-yellow color. BT was also porous in nature, sharp and angular in texture, and particle sizes retained on a U.S. No. 10 sieve appeared shiny or glassy. Smaller particles of BT were not as durable as those found in HBT or HRT. Percent water absorption, specific gravity, and grain size distribution for BT are given in Table 3.3.

BT are currently sold to other commercial smelting firms for removal of metals other than zinc products. The economic feasibility of using BT as a road construction aggregate as opposed to its utilization for additional smelting was not considered in this study.

The remaining Blackwell Zinc Company waste material to be studied was called Blackwell Condenser Tailings, hereafter termed BCT. BCT,

TABLE 3.3

Physical Properties of Test Materials

Test				To	ain Size otal Per	Distrib cent Pas dard Sie	ution sing			Bulk Specific	Percent Water
Material	1/2"	3/8"	No. 4	No. 10	No. 20	No. 40	No. 80	No. 100	No. 200	Gravity	Absorption
HRT	99.7	95.3	90.2	59.6	24.5	10.9	4.0	3.0	1.6	2.86	3.78
нвт	99.1	96.2	69.8	31.9	11.5	4.4	1.6	1.2	0.7	2.37	4.87
BT	100.0	99.7	90.4	64.2	29.7	10.1	2.4	1.7	0.8	3.14	5.00
вст	100.0	100.0	98.7	85.6	41.1	23.9	12.5	9.4	4.9	2.18	3.41
SS	100.0	100.0	100.0	100.0	100.0	100.0	87.0	35.4	13.1	2.66	
RS	100.0	100.0	99.0	87.0	67.1	36.9	4.1	0.5	0.2	2.63	

HBT - Retained - U.S. No. 4 HBT - Passing - U.S. No. 200 HBT - Retained - U.S. No. 20 HBT - Retained - U.S. No. 10

Figure 3.2. Sized Particles of Henryetta Black Tailings Illustrating Shape and Sharp Texture

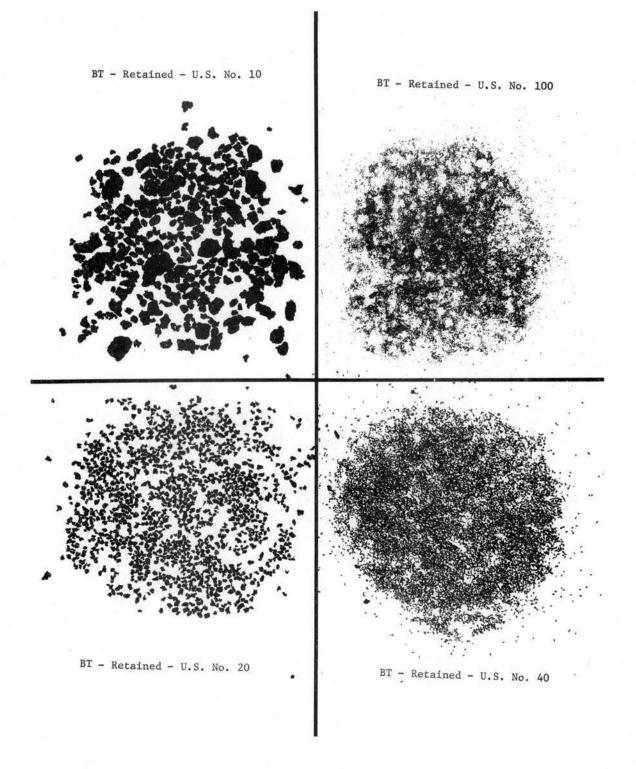


Figure 3.3. Sized Particles of Blackwell Tailings Illustrating Shape and Sharp Texture

as shown in Fig 3.4, was also a cohesionless material, white in color and relatively fine-grained as shown in Table 3.3. BCT, like the other waste materials studied, has a cubical shape and sharp angular texture, but was non-porous. The smelting process undergone by all waste materials is not described in this report, as it was considered privileged information by both companies providing slag for analysis.

Other cohesionless aggregates utilized during the investigation were two naturally occurring sands. One fine, poorly-graded sand, locally called "blow sand" but herein called Sapulpa Sand or SS, was obtained from a site located four miles west of Sapulpa, Oklahoma. SS was utilized as a substituted fine aggregate for the asphaltic part of the study. A coarse, well-graded sand herein called River Sand or RS was obtained from the Dolese Concrete Company of Stillwater, Oklahoma. This washed sand is widely used in local Portland cement concrete construction and is obtained from gravel/sand deposits near Ponca City, Oklahoma. RS was used as a "control" aggregate in the Portland cement phase of the investigation. Grain size distributions for both SS and RS are given in Table 3.3.

Cement utilized during the Portland cement study phase was Portland cement, Type I, while during the asphaltic phase of the investigation an asphaltic cement furnished by the Allied Material Corporation, Inc., of Stroud, Oklahoma, was used. This material had a Standard Penetration of 85-100 at 77°F.

The specific gravity of the asphaltic cement was 1.02 and was determined by procedures conforming to AASHO T 43 or ASTM D 70 specifications.

BCT - Retained - U.S. No. 20 BCT - Retained - U.S. No. 10 BCT - Passing - U.S. No. 200

Figure 3.4. Sized Particles of Blackwell Condernser Tailings
Illustrating Shape and Sharp Texture

CHAPTER IV

TESTING PROCEDURES

General

The investigation of zinc smelter waste usefulness was divided into three phases: use of each aggregate in asphaltic concrete, Portland cement concrete, and stabilized aggregate base.

Use of Zinc Smelter Waste as an Aggregate
in Sand-Asphalt Mixtures

The objective of the asphaltic concrete phase was to determine the feasibility of using zinc smelter waste as an aggregate in sand-asphalt mixtures. Hot mix/hot laid sand-asphalt mixtures are generally used in base course construction, but can be used as a surface course for pavements carrying limited light loads. Sand-asphalt obtains its name from the finer grained aggregate utilized in the mixture.

Gradation requirements for Sand-Asphalt Base Courses (hot mix-hot laid) conforming to Section 708A of the Standard Specifications for Highway Construction of the Oklahoma State Highway Commission are illustrated in Fig 4.1. No type of smelter waste tested had a natural gradation within specification limits. Therefore it was necessary to add additional fines in the form of SS (fine sand).

In the process of combining the tailings and SS, a maximum amount of smelter waste was used. A "midpoint" gradation was not

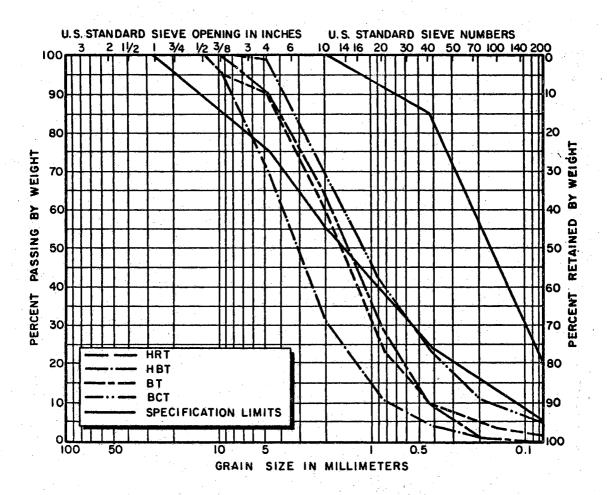


Figure 4.1. Grain Size Distribution Curves for Smelter Wastes and Specification Limits for Sand-Asphalt

achieved. Table 4.1 presents the percentage used of each smelter waste and SS. Figure 4.2 illustrates the resulting gradations of each combination of smelter waste and SS.

The Hveem-Gyratory Method of mix design was used during the study, conforming to the procedures as outlined in Part II, Test and Method Tex-206-F, September, 1966, Texas State Highway Department Materials and Test Division.

The specific gravity of the compacted Hveem specimens was determined using a modification of the procedure outlined in AASHO T166 or ASTM D1188. The procedure was modified by not allowing the specimens to cool to a temperature of 40°F for 30 minutes before the paraffin coating was applied. Instead, the samples were coated with paraffin at room temperature.

Testing procedures for the Hveem specimens followed a modification of ASTM D1560. The test was modified by not conducting the cohesiometer portion of the test.

Mix design procedures were followed using percentages of smelter waste and SS, then repeated using 100% smelter waste. Smelter wastes were mechanically ground to yield the same gradation produced by the addition of fine sand (SS).

Use of Zinc Smelter Waste as a Fine Aggregate in

Portland Cement Concrete

At the onset of the Portland cement concrete study phase, a concrete mix design was tried for each smelter waste, using Standard Specifications of the Oklahoma Highway Commission for Highway Construction. Sections 414.04 and 703.01 were used to mix design

TABLE 4.1

Percentages of Smelter Waste and Sapulpa Sand

Used for Sand-Asphalt

Name of Smelter Waste	Percentage of Smelter Waste Utilized	Percentage of Sapulpa Sand Utilized
HRT	55	45
нвт	60	40
BT	50	50
BCT	80	20

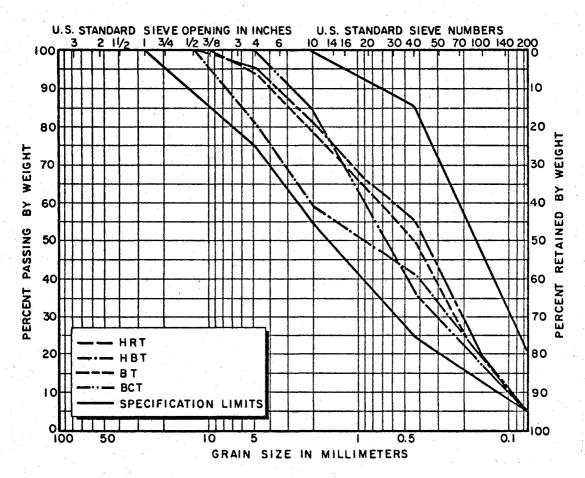


Figure 4.2. Grain Size Distribution Curves for Combined Tailings/Sand Mixtures and Specification Limits for Sand-Asphalt

requirements and gradation control. Figure 4.3 illustrates grain size distribution curves for each smelter waste compared to the specification limits for fine aggregates in Portland cement concrete. Physical property data presented in Chapter III was also used in the designs.

During this phase it was originally intended to design a mix for each smelter waste (combined with SS and/or RS to produce desired gradations) and compared strength relationships at 7, 14, 21, and 28 days with a control aggregate (RS) at the same gradation and mix design. However, the smelter waste mixes would not set, even after long-term curing, therefore the testing procedure was altered to determine the cause of Portland cement setting retardation.

An aggregate-cement reaction was the reason suspected for setting retardation of the mix. To substantiate this belief, test procedures were followed for determining the alkali reactivity of the aggregates, conforming to ASTM C289.

Results of this test indicated the smelter wastes were highly reactive, thus the concrete study phase was concluded. Additional details will be described in Chapter V of this report.

Use of Zinc Smelter Waste as a Fine Aggregate in Aggregate Base Courses

Smelter waste for use in a stabilized aggregate base course was evaluated qualitatively. Results of the previously described physical property tests were also used during this phase of the investigation.

Sections 303A, 303B, and 303C of the Standard Specifications for Highway Construction of the Oklahoma Highway Commission were used as guides for testing and evaluation.

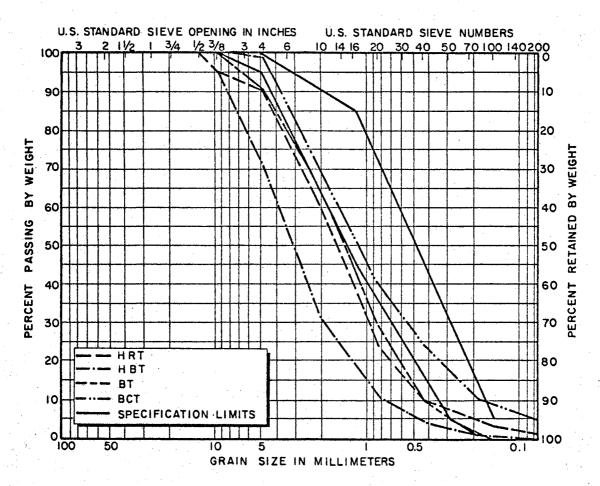


Figure 4.3. Grain Size Distribution Curves for Smelter Wastes and Specification Limits for Fine Aggregate in Portland Cement Concrete

CHAPTER V

EVALUATION OF TEST RESULTS

Asphaltic Concrete Study

Two mix designs for a hot-mix/hot-laid sand-asphalt base course were conduced on each type of smelter waste. The first mix design involved a combination of smelter waste and SS. The second mix design utilized 100 percent smelter wastes, with larger waste sieve fractions being ground to smaller sizes, to provide needed fine material.

Test results for two different types of smelter waste should not be compared with each other. It would be permissable to compare results of a particular waste used both in a 100 percent form and with the combination of SS.

Results of laboratory mix designs for all test mixes are summarized in Table 5.1.

Figures 5.1 through 5.4 illustrate the relationship between Hveem stability and asphalt content as computed by a total mix weight basis.

Figures 5.5 through 5.8 illustrate relationships between asphalt content and percentage of total voids. Figures 5.9 through 5.12 illustrate relationships between asphalt content and the unit weight of the compacted mix.

Figures 5.1 through 5.4 show a very interesting phenomena. A small difference of only three to five percent in Hveem stability can

TABLE 5.1

Hveem Gyratory Mix Design Results Summary

Test Material	Optimum Asphalt Content - Percent	Stability - Percent	Unit Weight lbs/cu ft	Void of Total Mix Percent
60% HBT + 40% SS	8	34.5	128.7	11.0
100% нвт	8	39.5	126.0	6.8
55% HRT + 45% SS	7	26.4	122.0	14.7
100% HRT	7	25.5	114.3	19.0
80% BCT + 20% SS	4	43.7	117.9	14.8
100% BCT	4	43.4	114.8	16.6
50% BT + 50% SS	6	37.7	139.4	16.5
100% BT	6	43	158.7	11.0

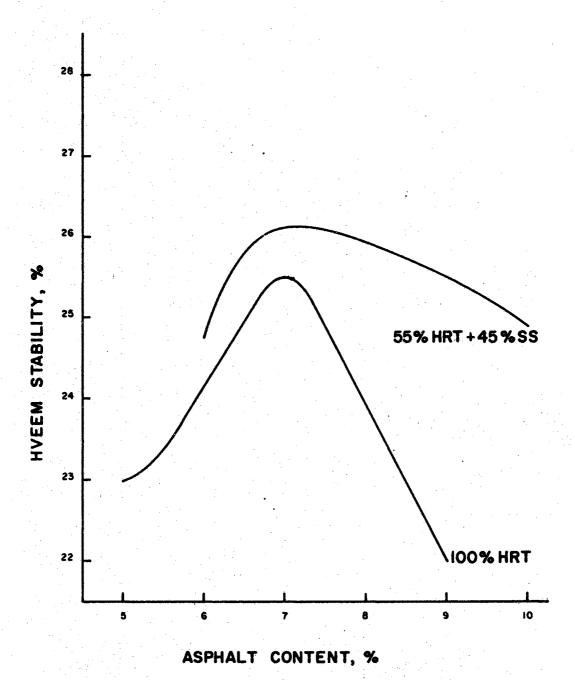


Figure 5.1. Hveem Stability and Asphalt Content Relationships for Henryetta Red Tailings

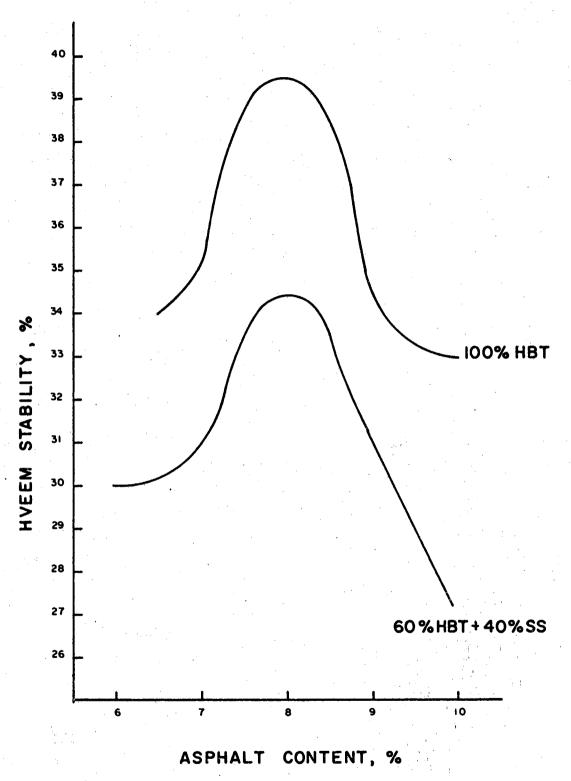


Figure 5.2. Hveem Stability and Asphalt Content Relationships for Henryetta Black Tailings

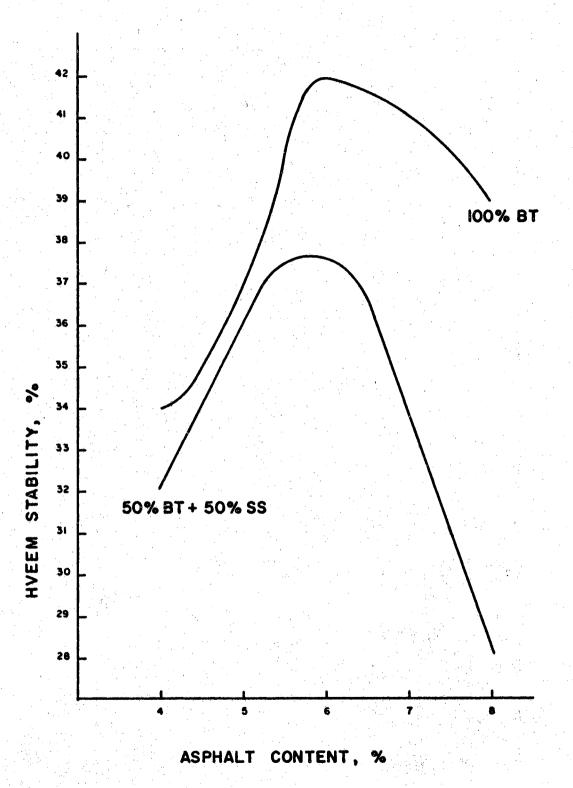


Figure 5.3. Hveem Stability and Asphalt Content Relationships for Blackwell Tailings

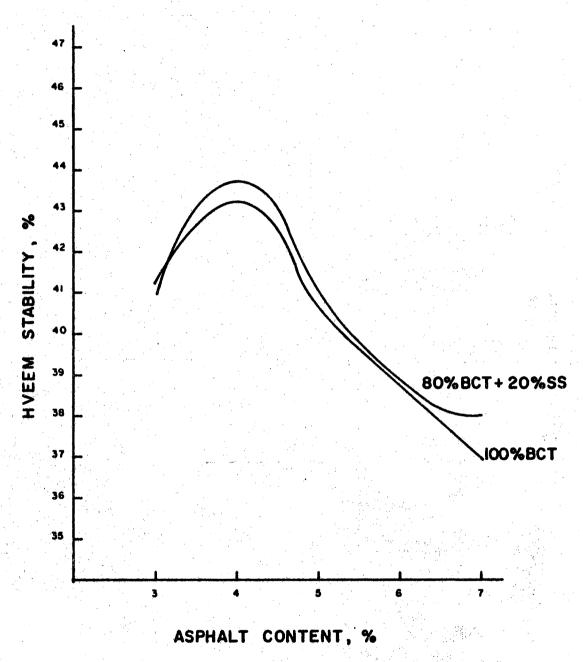


Figure 5.4. Hveem Stability and Asphalt Content Relationships for Blackwell Condenser Tailings

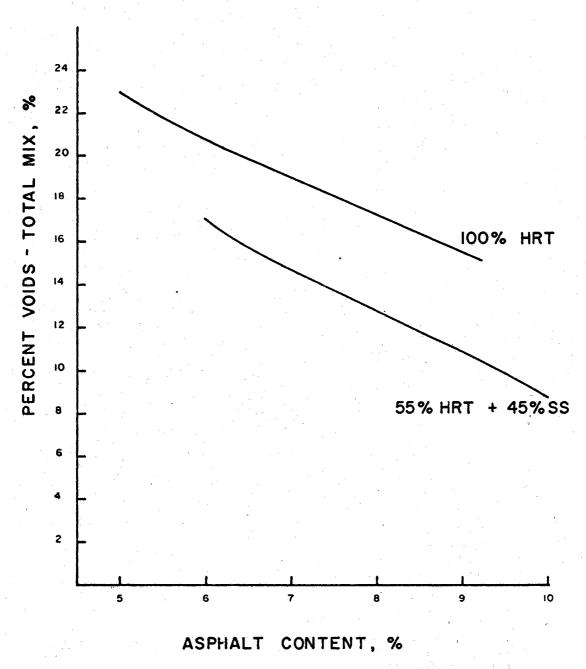


Figure 5.5. Percent Voids and Asphalt Content Relationships for Henryetta Red Tailings

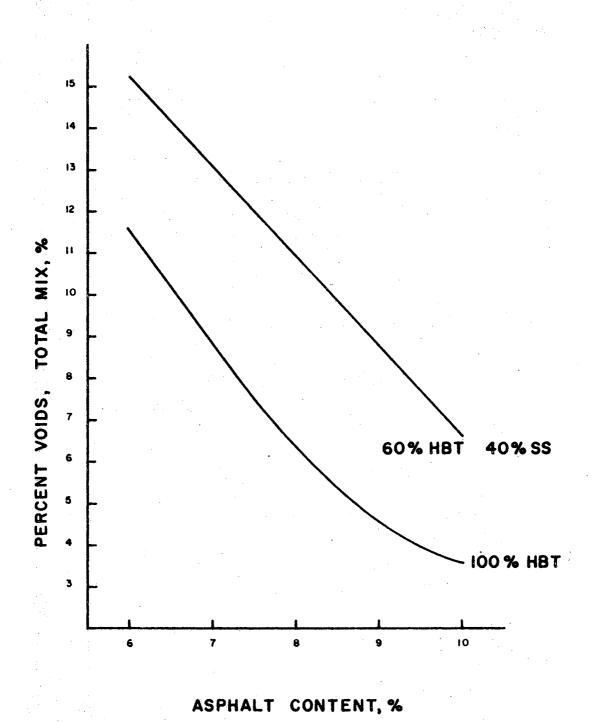


Figure 5.6. Percent Voids and Asphalt Content Relationships for Henryetta Black Tailings

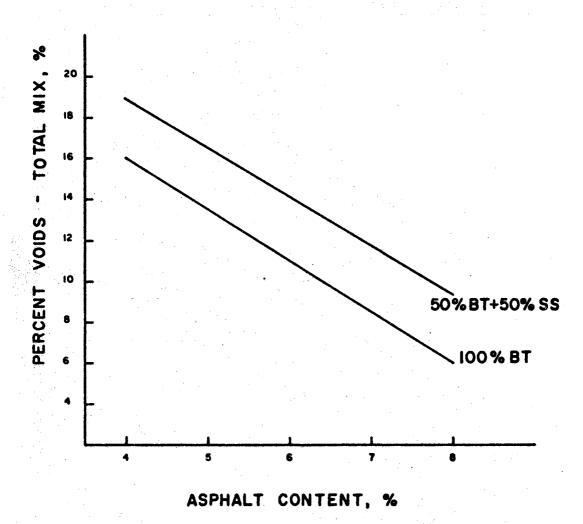


Figure 5.7. Percent Voids and Asphalt Content Relationships for Blackwell Tailings

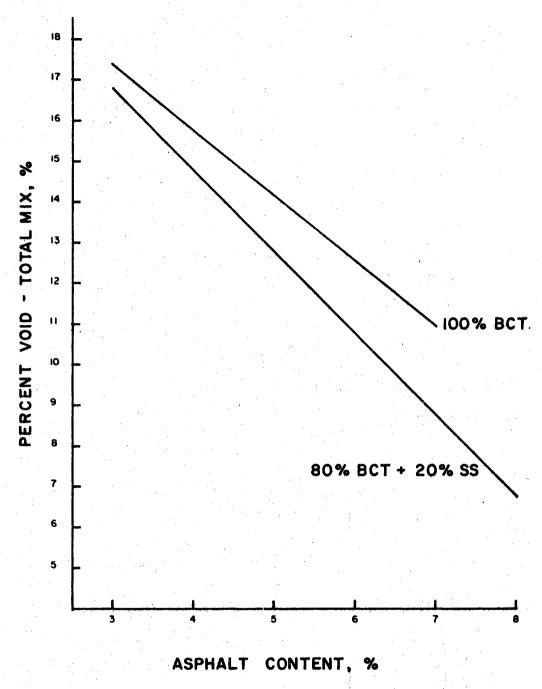


Figure 5.8. Percent Voids and Asphalt Content Relationships for Blackwell Condenser Tailings

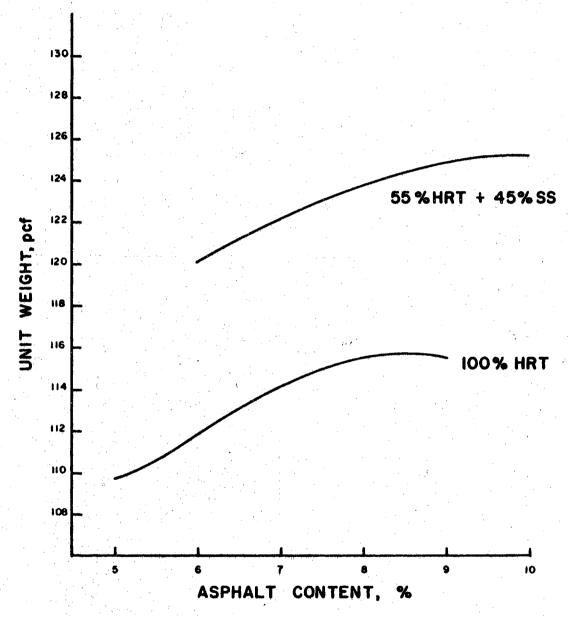


Figure 5.9. Unit Weight and Asphalt Content Relationships for Henryetta Red Tailings

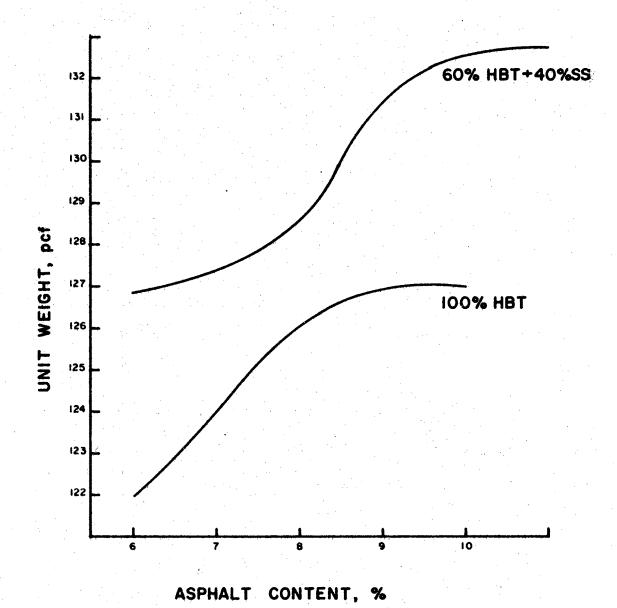


Figure 5.10. Unit Weight and Asphalt Content Relationships for Henryetta Black Tailings

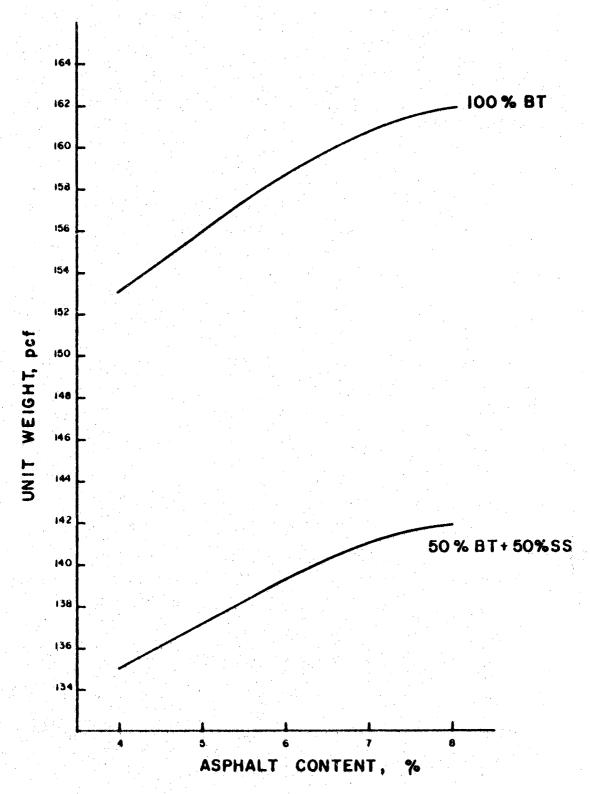


Figure 5.11. Unit Weight and Asphalt Content Relationships for Blackwell Tailings

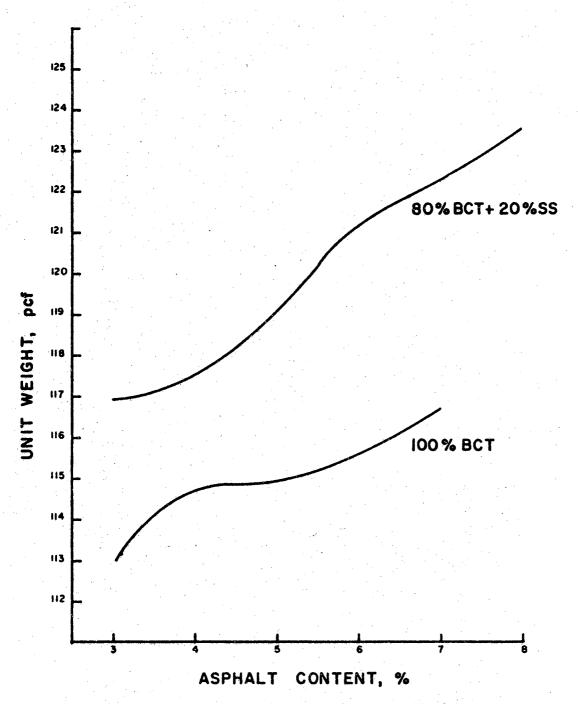


Figure 5.12. Unit Weight and Asphalt Content Relationships for Blackwell Condenser Tailings

be observed for an increase of one percent asphalt content. This is somewhat unusual, as a percentage difference in Hveem stability of as much as ten percent would be expected with conventional aggregates.

Meredith (Ref 2) reports a lack of response of density, stability, and flow in shell-asphalt mix designs as determined by the Marshall Method. Because of this problem, much emphasis is placed on the percentage of voids for the total mix. Earle (Ref 13) also mentions problems in determining asphalt contents using the Marshall test with blast furnace slag. Engineering judgment coupled with a proven field mix is generally used in slag-asphalt mix designs in Great Britain.

The largest difference in stability values between the various smelter wastes were obtained with larger percentages of SS. This is shown in Fig 5.3 (50% SS) and Fig 5.4 (20% SS).

The stability values occurring at the optimum asphalt content for smelter waste/sand asphalt and 100% smelter waste asphalt exceed the minimum 20% stability required by the Oklahoma Highway Commission's specifications for sand-asphalt mixtures, as obtained values ranged from 25.5 to 43.7 percent (see Table 5.1). Use of either 100% smelter waste or smelter waste/sand did not greatly affect obtained stability for a given smelter waste.

The unit weights of the compacted samples (110-130 pcf for all except BT) tend to be lower than usual for conventional aggregates, primarily because of low zinc waste specific gravities. Unit weights of approximately 140 lbs/cu ft can be expected from asphalt samples containing aggregate with a specific gravity of 2.65.

The compacted unit weight is less than 82 percent of the maximum theoretical density. The probable reason causing this behavior was the

high angle of internal friction of the zinc tailings.

Optimum asphalt contents for the mixtures were within the allowable range of 3.0-8.0 percent required by the Oklahoma Highway Commission.

It would be difficult to estimate the true quality of the Hveem Gyratory mix design method without a field test. However, it is the opinion of the authors that the test is adequate for determining the optimum asphalt content for an asphalt mixture containing waste zinc tailings.

Test results imply zinc smelter wastes can be substituted for conventional aggregates in hot mix/hot laid sand-asphalt base courses. It is the authors' opinion that the smelter waste could be used as fine aggregate in surface courses requiring an increase in aggregate size as compared to the finer grained mix of the sand-asphalt.

Portland Cement Concrete Study

The purpose of the concrete study was to procude a mix design consisting of cement, smelter tailings, and necessary additional limestone aggregate or course-grain sand, depending on grain size distribution requirements. The mix design was to be compared with the control aggregate RS to determine strength relationships.

Results were not obtained during the test for two reasons, non-uniform consistency of concrete and aggregate reaction with the cement paste. During the laboratory mix design, it was noted the smelter waste and the control aggregate, when mixed at the same aggregate gradation for a common mix, would not yield a common uniform consistency. Slump tests for HRB and HBT, yielding the desired one-half inch to one and one-half inch range (as required by

the 1959 Standard Specifications for Highway Construction for the Oklahoma State Highway Commission) could not be obtained without exceeding the specified water/cement ratio. Excess water was observed emerging from the bottom of the mix after the slump cone removed, but no appreciable amount of slump was noticed. At the same time, individual aggregate grains were observed to have an insufficient cement-paste coating although the mix did not slump. When the control aggregate was mixed at the same net water content, a slump greater than four inches was observed. The reason attributed for this zinc waste phenomena was the high angle of internal friction the materials were believed to possess.

The other problem encountered during the study was the reaction between aggregate and cement paste. When the BT and BCT were mixed, the non-uniform consistency problem was noticed, but a more severe problem of the mix not properly setting was observed. As the tailings were mixed with the water and cement a fluid resembling an "oily substance" would appear on the surface and would not mix with water. (Note: the tailings do not contain an "oily substance", the phenomena is merely described as such.)

When the mix was allowed to cure for up to forty-eight hours, it still had not taken its "initial set" and would appear to be very moist. When the concrete cylinders were removed from the molds and allowed to "field cure" in the laboratory for periods of 7 and 28 days, one could easily crush the samples in his hand, thus illustrating the poor qualities of the mix.

Retardation of setting observed during the study resembles that described by Schaffer and Peyton. Schaffer, in 1932, (Ref 14)

described problems experienced in England with efflorescence and scaling of concrete from release of water soluble substances by aggregates. Peyton (Ref 15) has reported that weathering of Sphalerite (ZnS) contained in chert aggregate in stockpiles produces zinc carbonate (smithsonite), which upon dissolution in the alkaline media of concrete causes excessive retardation of setting if present in more than 0.3 percent by weight of the cement.

To determine the cause of the retardation observed in the laboratory the previously described chemical test for determining the potential reactivity of aggregates was followed. Results of the test are based on the amount of reduction in alkalinity of the aggregate reacting with a sodium hydroxide solution under controlled laboratory conditions. However, results of the test were not a reduction in alkalinity but rather an increase in alkalinity. Another observation during the test was the formation of zinc hydroxide, a white flocculent precipitate formed by treating a solution of zinc salt with an alkali. The compound is almost insoluble in water, but is readily soluble in acids and in an excess of alkalies.

Assuming zinc carbonate was present in the aggregate, the following equation represents the reaction that occurred with the addition of sodium hydroxide:

$$ZnCO_3 + 2NaOH \rightarrow Na_2CO_3 + Zn(OH)_2$$

Both sodium carbonate and zinc hydroxide formed by the reaction are basic, explaining the increase in alkalinity observed during the reactivity test.

To further prove that zinc carbonate was present, a hydrochloric acid solution was added to the BT and BCT. This resulted in the formation of zinc chloride, as explained by the equation:

$$ZnCO_3 + 2HC1 \rightarrow H_2CO_3 + ZnC1_2$$

These results imply that BT and BCT contain smithsonite (zinc carbonate), which was responsible for retardation of concrete setting. Therefore, the zinc smelter waste should not be used as fine aggregate in Portland cement concrete.

Stabilized Aggregate Base Course Study

The stabilized aggregate base course phase of the investigation involved the feasibility of using Oklahoma zinc smelter waste in the construction of stabilized aggregate base courses.

Stabilized aggregate base courses, as defined by the Oklahoma State Highway Commission Specifications, are subdivided into three classes, I, II, and III. The primary differences between Classes are the methods of mixing, spreading, and the basis for payment. These items, although important, were not studied during the investigation.

The base course, according to the specifications, should consist of blended coarse aggregate, sand, stone dust, or other inert finely divided mineral matter and a soil binder. At least forty percent of the total mix retained on the No. 4 sieve was to be uniformly graded. Material passing the No. 40 sieve was required to have a plasticity index of six or less and a liquid limit of 25 or less.

Gradation of all three classes are divided into two types,

Type "A", and Type "B". Table 5.2 gives the gradation requirements

for the two types.

Figure 5.13 illustrates specification limits for Type "A" and grain size distributions for the four smelter waste.

Figure 5.14 also indicates the grain size distribution curves for the smelter wastes and specification limits for Type "B" stabilized aggregate.

Figures 5.13 and 5.14 indicate all four types of smelter tailings need additional course-grain gravels in order to meet requirements for either type of stabilized aggregate. Although the tailings do not meet specification requirements they do satisfy all other requirements set forth by the Oklahoma State Highway Commission.

It is a common procedure to blend aggregates on the job site to produce the required gradation. Therefore the smelter waste could be used in stabilized aggregate.

A lack of vegetative cover was observed near stockpiles of the smelter wastes tested. Soluble zinc leaches into the soil, and may destroy vegetation. This may or may not be desirable when the tailings are used in stabilized aggregate, but may not be of major importance when used under the center section of a road with wide surfaced shoulders.

Except for this possible problem, zinc smelter wastes are believed to be excellent sources of fine aggregate for use in stabilized aggregate base courses.

TABLE 5.2

Oklahoma State Highway Commission Specifications for Types

"A" and "B" Stabilized Aggregate Base Course

Sieve Size (Square)	Percent Passing		
	Type "A"	Type "B"	
3"	100%	100%	
1 1/2"	100%	40 - 100%	
3/4"	40 - 100%	30 - 75%	
3/8"	30 - 75%	25 - 60%	
#4	25 - 60%	20 - 50%	
#10	20 - 43%	15 - 35%	
#40	8 - 26%	7 - 22%	
#200	4 - 12%	3 - 10%	

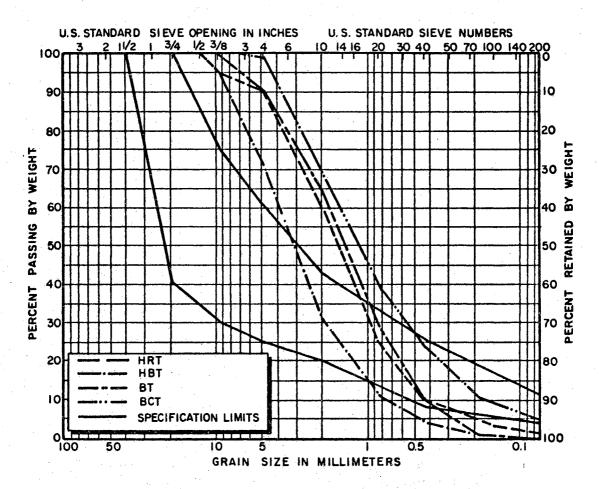


Figure 5.13. Grain Size Distribution Curves for Smelter Waste and Specification Limits for Type "A" Stabilized Aggregate

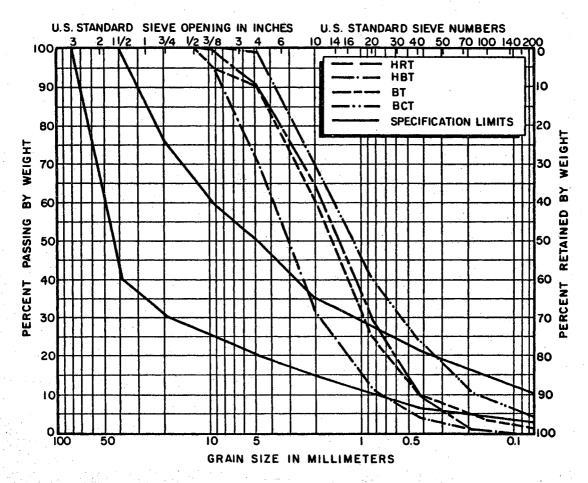


Figure 5.14. Grain Size Distribution Curves for Smelter Waste and Specification Limits for Type "B" Stabilized Aggregate

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

General

Results of the feasibility study for the use of zinc smelter wastes in highway construction indicate that the tailings may be used as aggregate in particular phases of road construction. Specifically,

- When natural gradation is modified by addition of fine sand or the material is crushed and recombined to meet particular gradation requirements, it may be used in sand-asphalt mixes. Resulting stability values are above minimums of the Oklahoma Highway Department and optimum asphalt contents are within specification limits.
- 2. The tailings should not be used as aggregates in Portland cement concrete because of cement-aggregate reactivity.
- 3. If the smelter wastes are to be used in stabilized aggregate base courses, additional course-grained aggregates must be added to meet particular gradation requirements.
- 4. When smelter wastes other than BCT are utilized in asphaltic pavement construction, higher bitumen contents can be expected.
- 5. The Hveem-Stabilometer test appears to be an adequate design method. However, the sharp angular texture of the aggregate, with resulting high angles of internal friction, cause unusual Hveem-Stability values.

6. The Marshall method of design appears to be greatly influenced by materials having high angles of internal friction and may not be satisfactory in determining optimum asphalt contents of the zinc tailings.

Recommendations for Further Research

Further research should be concerned with the asphalt study phase. Consideration should be given to stripping, degradation, weathering, and validity of mix design procedures. A relationship between field experience and laboratory mix design should be established. In addition, other types of zinc smelter waste (of which several exist in Oklahoma alone) should be investigated using the procedures described herein. The wide variation in physical properties of the four samples used in this study indicate that generalization of results should not be attempted.

Although this study was merely to determine feasibility of "untried" aggregates, results seem favorable for their usage as an aggregate in asphalt base construction, particularly since the materials are not presently being used and, in fact, constitute a serious pollution problem in their present condition and location.

REFERENCES

- 1. Hartherly, L. W., Asphalt Road Materials, Edward Arnold Ltd., London, 1967.
- 2. Meredith, E. C., "Utilization of Reef Shell in Flexible Pavement Construction in the Gulf Coast Area," <u>Proceedings</u>, <u>Association of Asphalt Paving Technologist</u>, 1958, pp. 323-356.
- 3. Verdros, P. J., "Investigation of Shell and Sand-Shell Mixes for Base Course," <u>Miscellaneous Paper No. 4-136</u>, Corps of Engineers, U.S. Army Waterways Experimentation Station, Vicksburg, Mississippi, 1955.
- 4. Bateman, J. H., "The Compressive Strength of Oyster Shell Concrete,"

 <u>Bulletin No. 29</u>, Louisiana State University and Agricultural
 and Mechanical College, College of Engineering, Engineering
 Experimentation Station, Baton Rouge, Louisiana, 1952.
- 5. Lee, A. R., "Slag for Roads Its Production, Properties, and Uses,"

 Journal of the Institution of Highway Engineers, Vol. 16,

 Number 2, February, 1969.
- 6. Mielenz, R. C., "Reactions of Aggregates Involving Solubility, Oxidation, Sulfates, or Sulfides," <u>Highway Research Board Record No.</u> 43, 1963, pp. 8-18.
- 7. Bauman, E. W., "Results of Aggregate Degradation Studies of Pennsylvania Turnpike Bituminous Surfacing, National Slag Association Technical Bulletin 102-24B, National Slag Association, 1961.
- 8. Crawford, C. M., Burns, K. N., "Building Damage from Expansive Steel Slag Backfill," <u>Journal of the Soil Mechanics and Foundation Division</u>, <u>American Society of Civil Engineers</u>, SM6, November, 1969, pp. 1325-1333.
- 9. Burnett, J. L., "Prospecting for Expansible Shale," Mining Engineering, Vol. 16, No. 1, January, 1964, pp. 50-51.
- 10. Horn, L. J., "Synthetic Aggregates Can Serve Effectively in Modern Highways," <u>Public Works</u>, Vol. 98, No. 11, November, 1967.
- 11. _____, "Try Adding Broken Bottles to Your Paving Mix," Better Roads, October, 1969, pp. 25-26.

- 12. Gray, D. H., "Properties of Compacted Sewage Ash," <u>Journal of the Soil Mechanics and Foundation Division</u>, <u>Proceedings</u>, <u>American Society of Civil Engineers</u>, SM2, March, 1970, pp. 439-451.
- 13. Earle, J. F., "All Slag Asphalt," <u>Roads and Road Construction</u>, Vol. 41, No. 487, July, 1963, pp. 206-209.
- 14. Schaffer, R. J., "The Weathering of Natural Building Stones,"

 Department of Scientific and Industrial Research, Building Research Special Report No. 18, 1932.
- 15. Peyton, R. L., "An Investigation of Crushed Flint Aggregates in Portland Cement Concrete," State Highway Commission of Kansas, Research Project No. 8001, 1945.

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