

**STUDIES OF THE THERMAL TRANSFORMATION
OF SYNTHETIC AGGREGATES
PRODUCED IN A ROTARY KILN**

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PREFACE

The primary objective of the synthetic aggregate research being conducted by the Texas Transportation Institute is to develop a recommended acceptance criterion for synthetic aggregates for use in all phases of highway construction.

This is the ninth report issued under Research Study 2-8-65-81, one of the synthetic aggregate research studies being conducted at the Texas Transportation Institute in the cooperative research program with the Texas Highway Department and U. S. Bureau of Public Roads. The first eight reports are:

"Correlation Studies of Fundamental Aggregate Properties with Freeze-Thaw Durability of Structural Lightweight Concrete," by W. B. Ledbetter, *Research Report 81-1*, Texas Transportation Institute, August, 1965.

"Effect of Degree of Synthetic Lightweight Aggregate Pre-Wetting on the Freeze-Thaw Durability of Lightweight Concrete," by C. N. Kanabar and W. B. Ledbetter, *Research Report 81-2*, Texas Transportation Institute, December, 1966.

"Aggregate Absorption Factor as an Indicator of the Freeze-Thaw Durability of Structural Lightweight Concrete," by W. B. Ledbetter and Eugene Buth, *Research Report 81-3*, Texas Transportation Institute, February, 1967.

"Flexural Fatigue Durability of Selected Unreinforced Structural Lightweight Concretes," by J. C. Chakabarti and W. B. Ledbetter, *Research Report 81-4*, Texas Transportation Institute, July, 1967.

"Suitability of Synthetic Aggregates Made from Clay-Type Soils for Use in Flexible Base," by W. M. Moore, Richard S. Van Pelt, F. H. Scrivner, and George W. Kunze, *Research Report 81-5*, Texas Transportation Institute, February, 1968.

"Performance Studies of Synthetic Aggregate Concrete," by C. E. Buth, H. R. Blank, and R. G. McKeen, *Research Report 81-6*, Texas Transportation Institute, March, 1969.

"Fundamental Factors Involved in the Use of Synthetic Aggregate Portland Cement Concrete," by W. B. Ledbetter, A. H. Meyer, and C. E. Sandstedt, *Research Report 81-7*, Texas Transportation Institute, November, 1969.

"A Sandblast Abrasion Test for Synthetic Aggregate Evaluation," by James T. Houston and W. B. Ledbetter, *Research Report 81-8*, Texas Transportation Institute, October, 1969.

In addition, a special report has been published under this research study.

The report is:

"A Recommended Synthetic Coarse Aggregate Classification System (Revised August 1969)," by W. B. Ledbetter, B. M. Gallaway, W. M. Moore, and Eugene Buth, *Special Report*, Texas Transportation Institute, August 1969.

The authors wish to thank all members of the Institute who assisted in this research.

The authors wish to acknowledge the guidance and assistance given by the advisory committee for this study. The members are as follows: (a) Texas Highway Department Personnel—Mr. Kenneth D. Hankins, Study Contact Representative and Research Area Representative; Mr. H. A. Sandberg, Jr., Materials and Tests Division Representative; and Mr. Louis White, Bridge Division Representative; (b) Bureau of Public Roads Personnel—Mr. Edward V. Kristaponis, Division Representative, and Mr. W. J. Lindsay, Regional Representative.

The opinions, findings, and conclusions expressed in this publication are those of the authors and not necessarily those of the Bureau of Public Roads.

ABSTRACT

The wide variations found in the properties of synthetic aggregates made from clay-type materials may be due in large part to differences in the degree of thermal transformation of their constituents resulting from processing in rotary kilns.

In order to study this problem, two different clays were processed in a research rotary kiln under different conditions of temperature and retention time. For each material, firing conditions were planned to yield two groups of aggregates, one heavy (more than 55 lbs. per cu. ft.) and one light (less than 55 lbs. per cu. ft.).

The raw clays and the resulting aggregates, as well as a commercial synthetic aggregate for comparison, were investigated by X-ray diffraction, differential thermal analysis (DTA), effluent gas analysis (EGA), and gas chromatography (GC). This combination of methods yielded useful information concerning the extent of the transformation of the clay minerals into new crystalline substances, the elimination of impurities (such as organic matter, carbonates, and sulfur compounds), and the gases responsible for bloating. From this information the poorly burned aggregates could be identified.

Retention time as well as temperature was shown to be important in bringing the thermal reactions to completion. The most effective combination of temperature and retention time depends upon the particular raw material. Firing conditions producing a lightweight aggregate do not automatically insure that the aggregate will be chemically and physically sound.

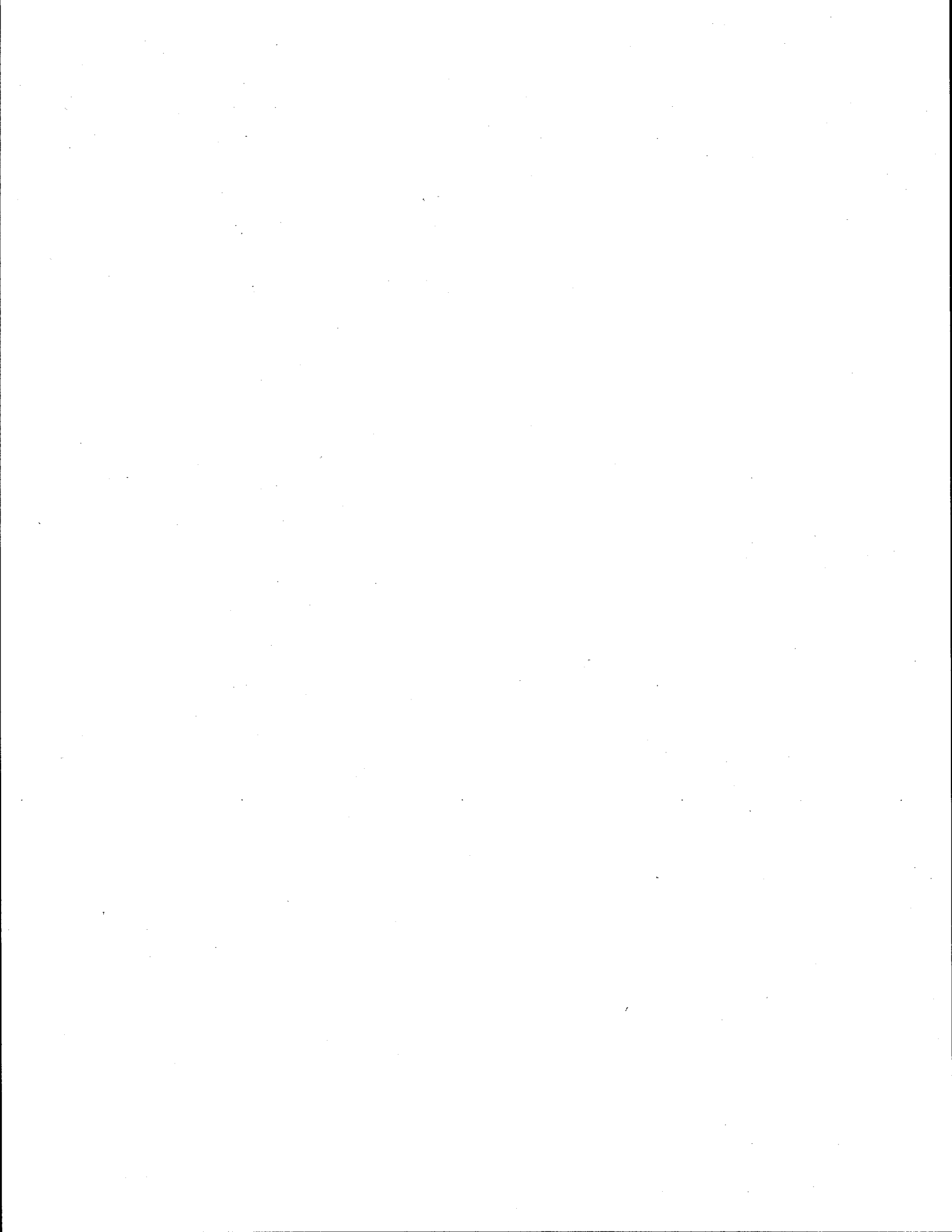
The effects of the degree of thermal transformation on the engineering properties of these aggregates, and on their behavior in concrete, are discussed in *Reports 81-8 and 81-10*.

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I. Introduction

1.1 General Statement

The accelerating demand for construction aggregates has resulted not only in the depletion of many sources of natural aggregates, but also has created a corresponding increase in the production of synthetic aggregates. Synthetic aggregates are defined here as the aggregate product resulting when shale, clay, or slate raw materials are calcined at temperatures usually in excess of 1500°F. Although synthetic aggregates have been in widespread use in the United States for the past ten to twenty years, there are many unresolved problems in reliably predicting the serviceability of any given aggregate. These problems are perhaps the consequence of the lack of a fundamental approach based upon an understanding of the thermal transformation processes which the material undergoes during manufacture, and which in large measure control the physical properties of the resulting aggregate.

1.2 Previous Work and Literature

The analysis and classification of natural aggregates for concrete have been studied by many people. Research in this area has resulted in quality-testing procedures, some of which have been standardized as ASTM test methods (1).^{*} But in general the use of these test methods has not produced completely reliable acceptance criteria for synthetic aggregates. This difficulty quite possibly stems from the fact that adequate performance records for the validation and modification of the test methods are practically non-existent for most synthetic aggregates. An equally important aspect is that the complex thermal transformations involved in the production of synthetic aggregates may well result in irregular aggregate behavior with respect to accepted testing procedures developed in general from experience with natural aggregates. In addition, a search of the literature has shown that minimal consideration has been given to any experimental program in which a primary consideration was the degree of thermal transformation of the raw materials during rotary kiln processing.

Perhaps the most often quoted study of the more readily determinable properties of synthetic aggregates was the work of Conley, et al. (2). Their report furnishes information concerning the effect of rotary kiln processing on the nature of bloating, thermal reactions, aggregate absorption, unit weight, chemical attack by acids and bases, and other miscellaneous aspects. Although the research described does not generally provide a usable criterion for aggregate acceptance, it does provide limited but helpful information on the use of research-sized rotary kilns for the production of synthetic

^{*}Numbers in parentheses designate references contained in Section V.

aggregates. A knowledge of manufacturing techniques and of the effect of the variables involved is a necessity for the effective production of synthetic aggregates in either a research-sized or commercial-sized rotary kiln.

Much literature has been published by the ceramic societies concerning the physical properties of fused silicates. For example, the work of Russell (3) presents a good summary of the thermal transformation processes and their effect on material imperfections, coefficient of thermal expansion, and freeze-thaw durability. However, the ceramic products and the thermal processing described are not directly relatable to synthetic aggregates of structural quality. Nevertheless, the fact that basic research in the ceramic field has greatly improved the effective manufacture and use of ceramic products emphasizes the need for similar studies in the synthetic aggregate area.

A recent study by Das (4) represents a more basic approach to the analysis of synthetic aggregates. Although he recognized the relationships between the transformation process and the physical behavior of the product, the application of his results is somewhat limited by the laboratory methods (such as muffle furnace) used for the thermal processing and the preparation of the raw sample.

1.3 Objectives and Scope of the Study

The conclusion reached from a consideration of the literature mentioned is that the most effective plan of research on the evaluation and classification of synthetic aggregates is one in which the aggregates are realistically processed and are characterized by various degrees of thermal transformation. In addition, the aggregate-evaluating tests should be closely related to appropriately selected conditions of field environments.

Accordingly, the larger study of which this report is a part attempted to:

1. Produce synthetic aggregates under a variety of known controlled conditions in a research rotary kiln.
2. Develop experimental methods for determining the degree of thermal transformation of the aggregates so produced. This aspect of the study is the subject of this report.
3. Determine by experimental methods the effect of the degree of thermal transformation on selected properties of the aggregates related to field environment. The results of these experiments are described in *Report 81-10*.
4. Propose tests, based on the methods used in the study, which hopefully will provide data for improved acceptance criteria for synthetic aggregates. One such test is described in *Report 81-8*.

II. Basic Properties of the Aggregates Studied

2.1 Raw Materials

Two different raw materials were used to produce a total of twelve aggregates for this study. In addition, a commercially produced aggregate with a good field performance record was used in parallel tests of this study in order to more meaningfully relate the over-all results to actual field performance.

The raw materials used are clays obtained by strip mining and are termed R and Z. They are illustrated in Figure 2-1.

Clay R is presently in commercial production and is mined in Eastland County, Texas, from strata of the Pennsylvanian system of the Paleozoic Era. Mining has reached a depth of about 100 feet from the surface. Although huge quantities of clay are present in this area, only a small portion existing in pocket deposits has the

desired properties needed for aggregate production. The desirable properties which characterize material R are its uniformity with depth, lack of thin bedding planes, low content of calcareous and sulfur-bearing compounds, excellent dry strength, resistance to degradation, and uniformity of texture.

Clay Z was mined in Ellis County, Texas, and comes from the Eagle Ford group of the Cretaceous system of the Mesozoic Era. This particular material has not been used for the commercial production of synthetic aggregates, although clays of the Eagle Ford group have been used elsewhere for this purpose. In its larger features the deposit does not appear to vary greatly, although its extent and uniformity have not been determined. Material Z is a calcareous clay, or marl, containing numerous calcareous marine fossils, large nodules of calcite and of calcareous siltstone, and a relatively high content of sulfur-bearing minerals. It has a closely spaced bedding structure, which under certain processing conditions tends to promote exfoliation.

2.2 Processing Parameters

The aggregate nomenclature, the rotary kiln processing parameters, and the resulting unit weights of the synthetic aggregates are given in Table 2-1. Three different retention times were used, and in general, temperatures were sought, depending upon the bloating behavior of each material, which would give aggregates having two different ranges of unit weights. The commercial aggregate studied was produced from material R, but complete details of its processing parameters are not available.

2.3 Unit Weights

The aggregates are designated according to their unit weights, those of the lighter group being given odd numbers, and those of the heavier group even numbers. In each weight category the progression of the numbers follows the increase in retention time (approximately 20, 35, and 48 minutes).

2.4 Surface and Pore Characteristics

Photographs showing the surface and pore characteristics of all the aggregates are given in Figures 2-2, 2-3 and 2-4. It will be seen that for aggregates R the lighter weight, more bloated aggregates generally show larger, less uniform pores and a greater degree of surface fusion than the heavier ones. On the other hand, aggregates Z are characterized by large blisters, irregular pore structure, and irregular surface fusion for all burning conditions. These properties are probably the result of the bedding structure and the nonuniform distribution of gas-forming constituents in the raw material. From this clay the production of an aggregate having uniform pore structure and a relatively impervious shell would probably be difficult.

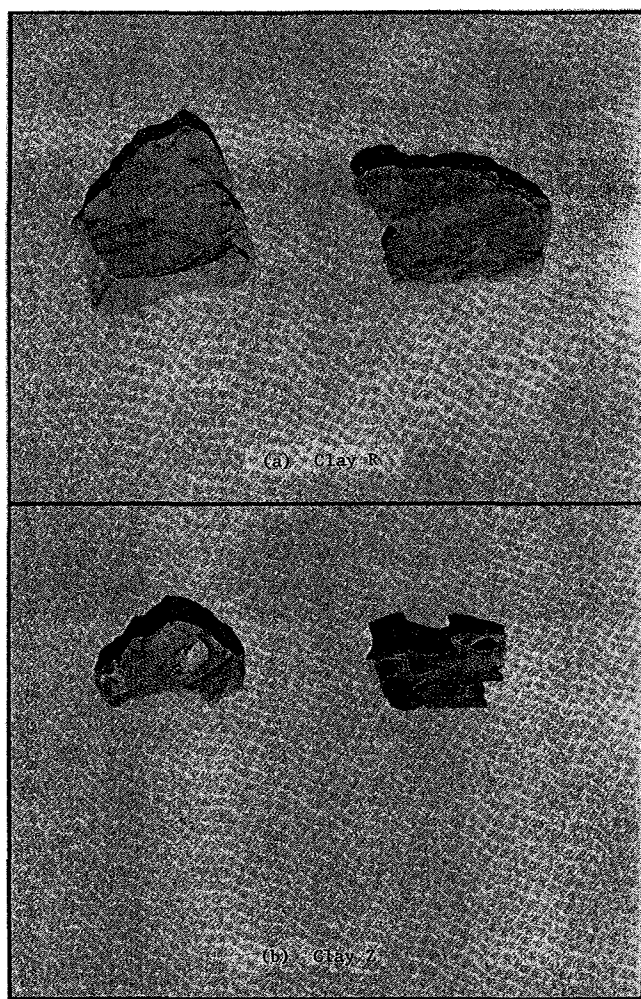


Figure 2-1. Clays used for the production of aggregates Z and R.

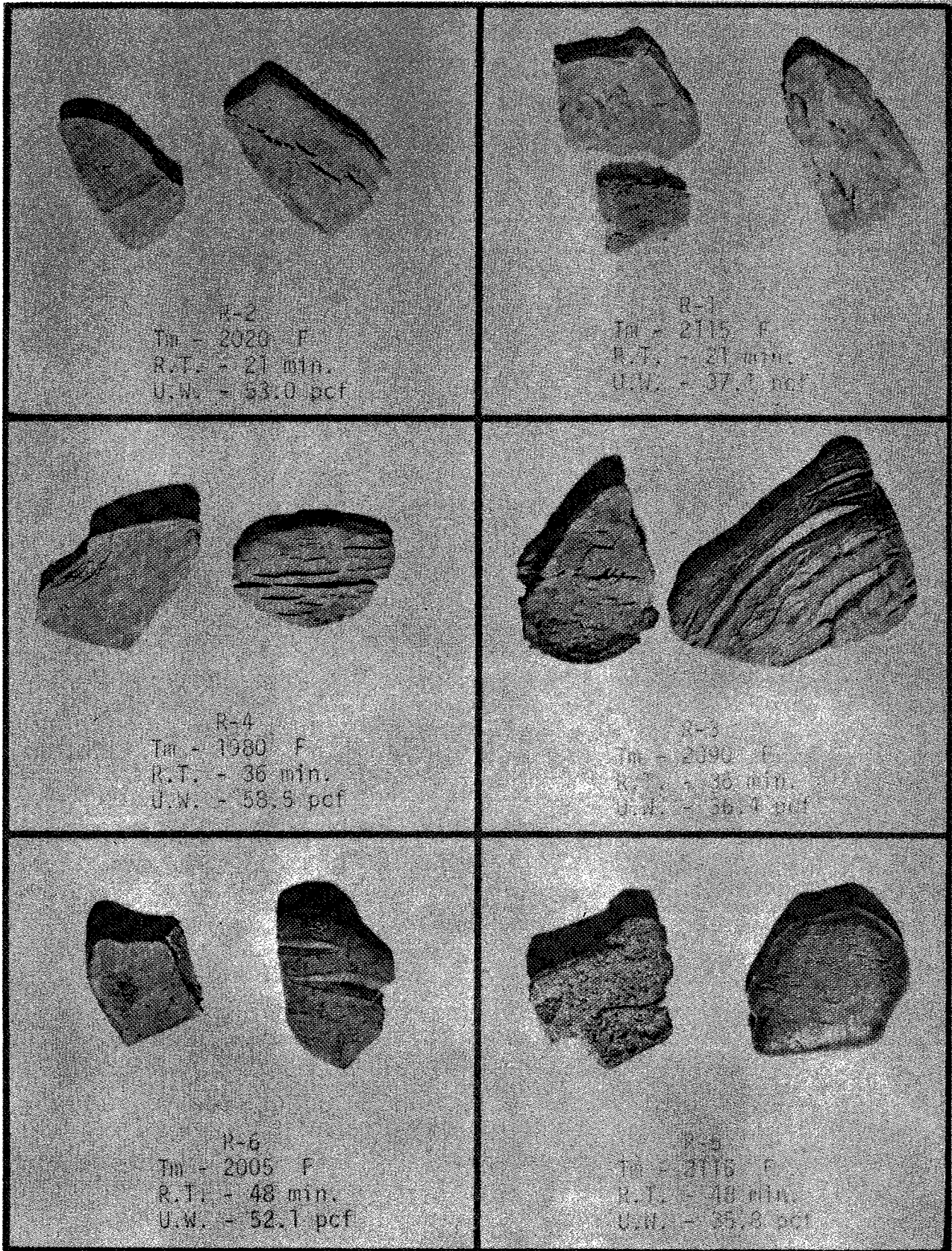
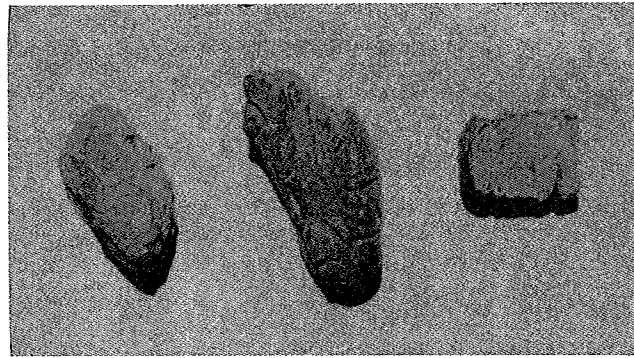


Figure 2-2. Surface and pore characteristics of pilot kiln aggregates R.



R—COMM.
 $T_M \approx 2000^\circ\text{F}$
 U.W.—48.1 PCF

Figure 2-3. Surface and pore characteristics of commercial aggregate R.

TABLE 2-1. PROCESSING PARAMETERS FOR AGGREGATES R AND Z

% Moisture* Raw Material Grading Raw Material Processing Parameters	Aggregates R						Aggregates Z						
	comm.	1	3	5	2	4	6	1	3	5	2	4	6
Raw Material	—	3.8%						11.5%					
Grading Raw Material	—	1 in.—#4						1 in.—#4					
Processing Parameters	comm.	1	3	5	2	4	6	1	3	5	2	4	6
Feed Rate (CFM)	—	.145	.090	.062	.145	.090	.062	.145	.090	.062	.145	.090	.062
Kiln Slope (in./ft)	—	.730	.433	.306	.730	.433	.306	.730	.433	.306	.730	.433	.306
Kiln Speed (rpm)	—	1.6	1.5	1.5	1.6	1.5	1.5	1.6	1.5	1.5	1.6	1.5	1.5
Retention Time R. T. (mins.)	—	21	36	48	21	36	48	20	34	48	20	34	48
Loading Factor (%)	—	3.9	4.1	3.9	3.9	4.1	3.9	3.8	3.9	3.9	3.8	3.9	3.9
Max. Temp.** T_M ($^\circ\text{F}$)	≈ 2000	2115	2090	2115	2020	1980	2005	2009	2035	2040	1712	1685	1850
Flame	—	oxidizing						oxidizing					
Unit Wt.*** U.W. (pcf)	48.1	37.1	36.4	35.8	53.0	58.5	52.1	33.4	34.2	32.3	46.5	50.4	42.5

*% Moisture determined by oven drying at 200°F for minimum of 24 hrs.

**Obtained by optical pyrometer readings.

***Tested and Graded according to midpoints of grading limits set for $\frac{3}{4}$ in. — No. 4 aggregates of ASTM C29 and C330.²

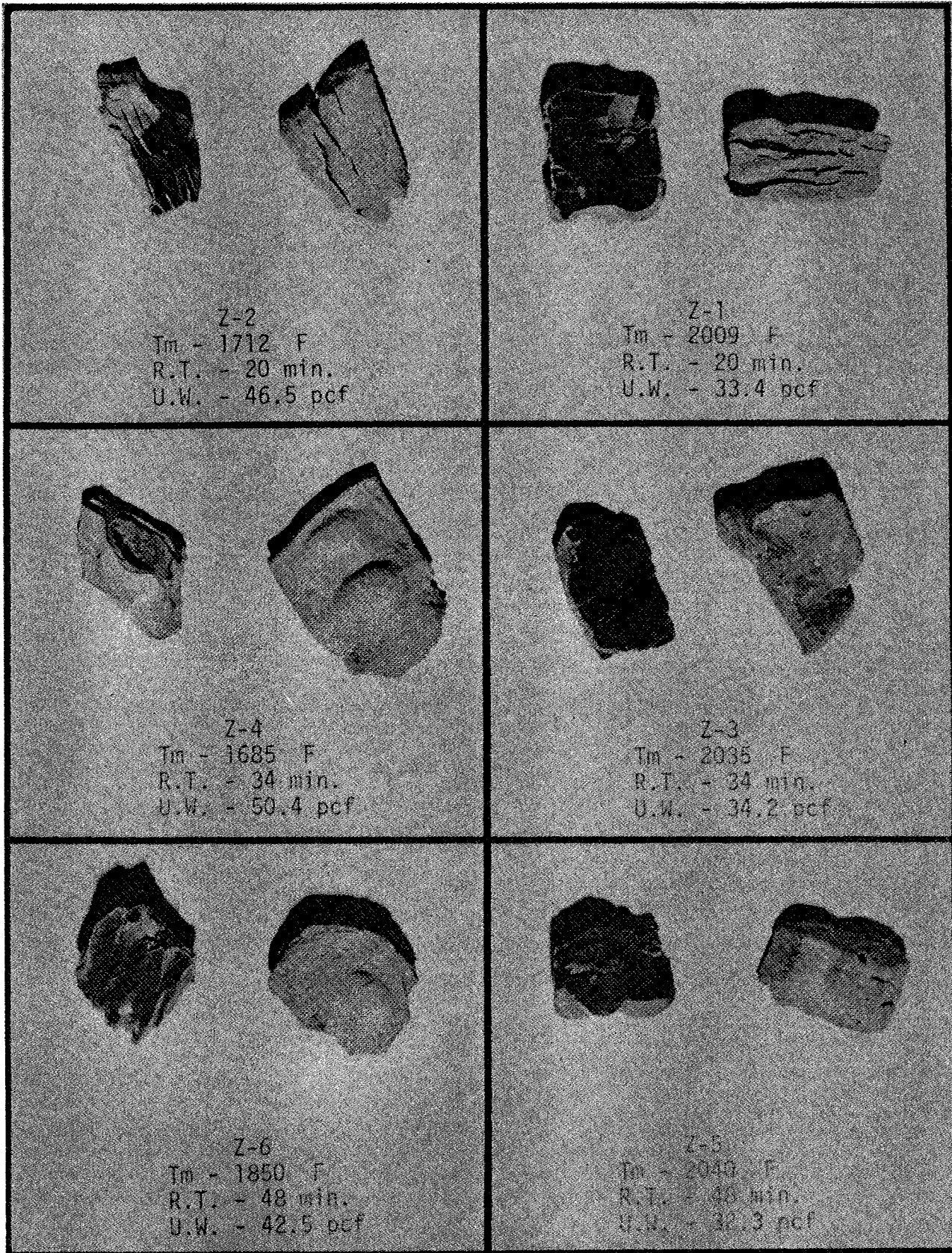


Figure 2-4. Surface and pore characteristics of pilot kiln aggregates Z.

III. X-Ray Diffraction Studies

3.1 General Statement

Four basic techniques were used for the study of thermal transformation characteristics of the aggregates, namely, X-ray diffraction, DTA,* EGA,** and gas chromatography. Although these methods of analysis are well known in materials research, their use in a research study of this type has received little attention. Fortunately, a great many soil characterization studies have been conducted with the aid of similar equipment, and as a result, its use in a study of thermally processed clay-type materials would seem quite logical and revealing. A better understanding of the transformations occurring during rotary kiln processing should result. In addition, a study of this type could perhaps define a point in the transformation process beyond which the durability of the aggregate could be assured.

3.2 Literature

The use of X-ray diffraction techniques in the study of various materials has been discussed in many papers and texts (4, 5, 6, 7, 8, 9, 10).

3.3 Sample Preparation

3.3.1 Raw Clays

The laboratory procedures*** used in this study for the preparation of the raw clays for X-ray diffraction analysis included the removal of soluble salts, carbonates, and organic matter. No treatment for the removal of iron oxides was used because their presence in significant quantity was not indicated by sample color. The raw materials were pulverized and sieved to a size of minus no. 100-mesh prior to the treatment described below.

3.3.1.1 *Dissolution of Soluble Salts*—Approximately 25 grams of sample was placed in a pyrex beaker with about 500 ml. of distilled water. The solution was stirred at intervals of 15 to 20 minutes for a period of two hours. A settling period of two hours was followed by decantation of the supernatant liquid. When the clay remained in suspension beyond the two-hour period, 1.0 N magnesium chloride was added in the minimum amount necessary to flocculate the clay. This entire treatment was repeated twice, because the presence of a small amount of gypsum in both R and Z clays had been indicated by earlier tests in which a separate portion of the supernatant liquid formed a precipitate upon the addition of an equal volume of acetone.

After the final decantation, the sample was transferred to two 250-ml. centrifuge tubes and centrifuged at 2000 rpm for 10 minutes. The supernatant liquid was then siphoned off. Next, the tubes were half filled with distilled water, stoppered, and shaken for five minutes in a reciprocating shaker. The centrifuging and

washing procedure was repeated until the clay remained in suspension after centrifuging. At this time several drops of 1.0 N magnesium chloride were added to the suspension, followed by additional centrifuging and decantation of the supernatant liquid. The sample was then transferred with the aid of a spatula to a 500-ml. beaker for removal of carbonates.

3.3.1.2 *Removal of Carbonates*—Approximately 100 ml. of 1.0 N sodium acetate, adjusted to pH 5 with acetic acid, were added to the beaker, which was then covered with a nonribbed watch glass. The effervescence indicated only a trace of carbonate in Clay R, but a considerable amount in Clay Z. The solution was next heated to a temperature of 80 to 90°C and stirred hourly for five hours, after which the supernatant liquid was siphoned off. A small portion of the sample taken from the coarser material was then treated with a few drops of 1:1 HCl. The lack of effervescence indicated that the carbonate removal was complete.

The sample was transferred to two centrifuge tubes half filled with distilled water and then centrifuged for five minutes at 2000 rpm. The supernatant liquid was then decanted, and the washing-shaking procedure was repeated as previously described. When the clay remained in suspension after centrifuging, several drops of 1.0 N MgCl₂ were added, and centrifuging was continued for 10 to 15 minutes. This operation was repeated until a clear supernatant liquid was obtained and then decanted. The sample was washed once more and transferred to a 600-ml. pyrex beaker for removal of organic matter.

3.3.1.3 *Removal of Organic Matter*—A soil to water ratio of 1:1 to 1:2 was obtained by heating the solution and evaporating a portion of the water. The suspension was made slightly acidic by adding a few drops of 1.0 N HCl and testing with litmus paper. A solution of 30 percent hydrogen peroxide was then added in increments of 5 to 10 ml. while the sample was stirred. Care was taken not to allow excessive effervescence. Once frothing had ceased, the sample was heated to about 65°C with continued stirring until effervescence had ceased once again.

The sample was next placed in centrifuge tubes and centrifuged for 10 minutes at 2000 rpm. The supernatant liquid was decanted, and the sample was washed with distilled water and centrifuged as before. This process was repeated until clay particles remained in suspension after centrifuging. At this time a few drops of 1.0 N MgCl₂ were added to the suspension, followed by centrifuging. The resulting supernatant liquid was decanted, and the sample was ready for final clay-particle extraction.

3.3.1.4 *Extraction of Minus-2-Micron Clay*—The sample was suspended in a solution of 100 ml. of 0.1 N calgon and about 1700 ml. of distilled water. A timed settlement procedure, based on Stokes' law, indicated that seven hours and thirty-five minutes were required for all particles greater than 2 microns in diameter to fall ten centimeters in water. Consequently, after this time, the liquid above 10 cm. depth contained only the

*Refers to differential thermal analysis throughout the text.

**Refers to effluent gas analysis throughout the text.

***Kunze, G. W., taken from unpublished laboratory methods used in Agro. 626 (Soil Mineralogy), Texas A&M University.

minus 2-micron clay particles and was siphoned off for X-ray study.

3.3.1.5 *Irradiation With X-rays*—The minus 2-micron fraction of the clay was divided into two portions; one was saturated with magnesium and the other with potassium, using the chloride salts. From each of these suspensions several drops were placed on glass slides and evaporated to thin films. These films were then subjected to X-radiation for determination of the crystalline minerals present. After the magnesium-saturated samples were irradiated, they were treated with an ethylene glycol spray and irradiated again. These saturation treatments were necessary because certain clay minerals exhibit common diffraction peaks under some conditions. By these treatments three X-ray patterns were obtained for each sample, and the effect of the different cation saturations on the basal spacings allowed the identification of the clay minerals.

3.3.2 Burned Aggregates

A representative sample of each of the thirteen rotary-kiln-produced aggregates of this study was selected for X-ray diffraction analysis. These aggregates consisted of relatively hard particles ranging in size from dust to one inch. They were pulverized and sieved to minus 100 plus 200-mesh size. These powdered samples were then placed in a sample holder with no other treatment and irradiated.

At the time the samples were prepared, it was thought that all clay minerals would be modified or destroyed by processing in a kiln, and that therefore no special procedures for their concentration and orientation would be required. Subsequent DTA and EGA studies, described in Section IV, indicated that this assumption may not have been entirely justified, and that clay minerals in some of the burned aggregates may have escaped detection by X-rays for this reason. In future studies, procedures for the concentration of any clay minerals remaining in burned aggregates should be used.

A more exacting technique for the preparation of powdered samples of kiln-fired materials has been reported by Brownell (8). This method involves the use of heavy media separation to isolate the mineral phases present. Although this method results in X-ray patterns that are more easily analyzed, the time-consuming procedures required are not always justified and were not used in the present study.

3.4 X-Ray Equipment Settings

A Norelco X-ray diffraction unit in the Department of Soil and Crop Sciences of Texas A&M University was used to analyze the samples. A description of the equipment and the conditions under which the analyses were made is given below:-

- 35,000-volt operating potential
- 30-ma operating current
- K α copper radiation, nickel filter
- 1° divergence slit
- 1° scatter slit
- 0.003-in. receiving slit
- 1° - 40° - 2 theta diffraction angle range

3.5 Interpretation of X-Ray Diffraction Patterns

The primary reason for the X-ray diffraction study of the aggregates was to detect the changes in the crystalline components of the material brought about by the various heating conditions. The results of this study are given in the forms of the X-ray patterns of Figures 3-1 and 3-2. In both figures the identified minerals are indicated, as well as the processing conditions of retention time and maximum temperature. Here also the aggregates are grouped according to unit weight classification and increasing retention times.

3.5.1 Raw Materials

The uppermost patterns of Figures 3-1 and 3-2 are those of the Mg-saturated, minus 2-micron fraction of the raw clays. From the positions and relative heights of these peaks it was possible to determine not only the identity of the clay minerals present, but also their relative quantities. The method used for the quantitative determinations is based on the general approach developed by Johns, et al., and extended by Kunze.*

X-ray diffraction analysis of raw material R (Figure 3-1) shows that the clay minerals chlorite, illite, and kaolinite make up 7, 62, and 31 percent, respectively, of the clay minerals in the minus 2-micron fraction. Considerable alpha quartz is also indicated, even in this fine fraction, but it was not quantitatively determined.

*Personal communication regarding standard practices used by Department of Soil and Crop Sciences, Texas A&M University.

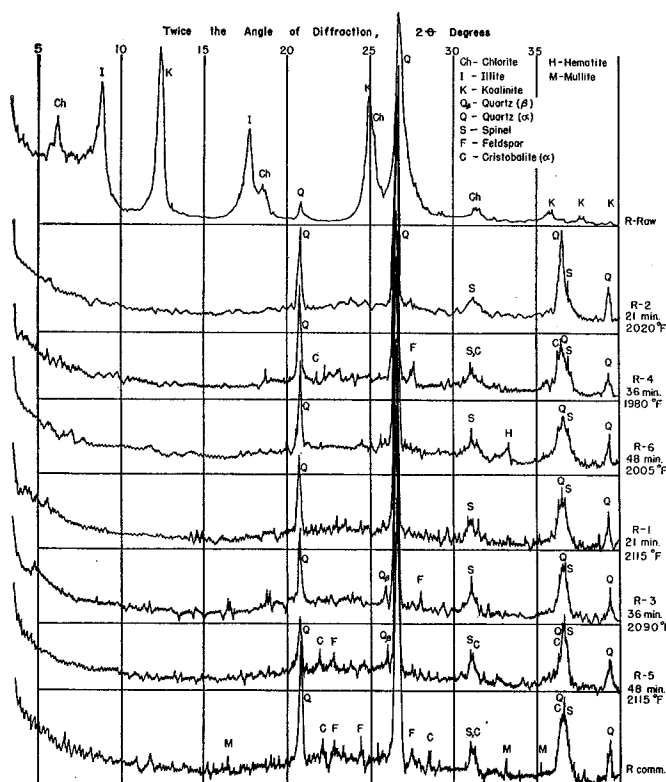


Figure 3-1. X-ray diffraction patterns for raw and burned aggregates R.

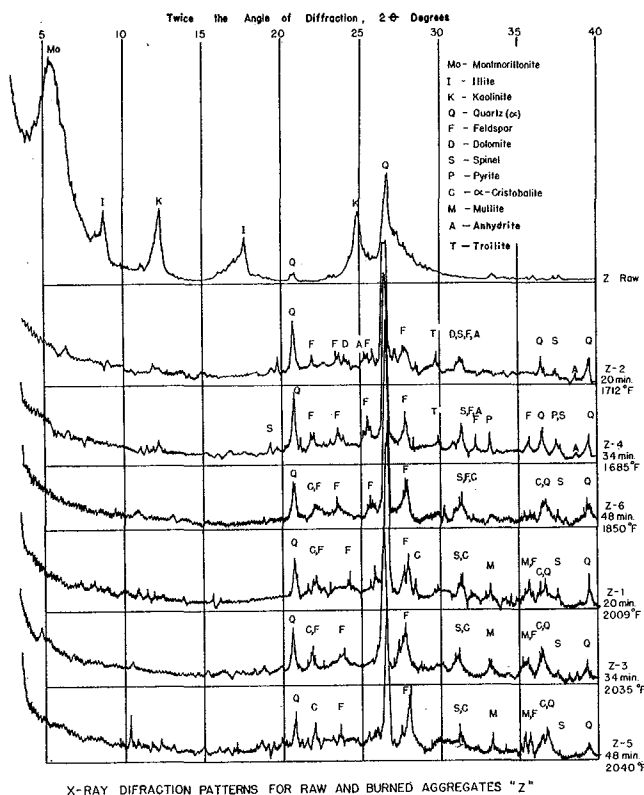


Figure 3-2. X-ray diffraction patterns for raw and burned aggregates Z.

In addition to these minerals, trace amounts of calcium carbonate and gypsum were detected in the original clay by the qualitative tests mentioned in Sections 3.3.1.1 and 3.3.1.2. These two minerals and perhaps others are not indicated by X-ray peaks because of their removal by the pretreatment procedure.

In raw material Z, Figure 3-2, illite, kaolinite, and montmorillonite make up 44, 27, and 29 percent of the clay minerals, respectively. The nonclay minerals are alpha quartz, as shown in Fig. 3-2, and much calcium carbonate and a little gypsum as indicated by the qualitative chemical tests.

To the writers' knowledge, there have been no widely accepted research studies which relate the mineral composition of the raw materials to the properties, other than bloating, of the resulting burned aggregates. There are several possible reasons for this lack of research. First, the differentiation of the various effects exerted by the components in mixtures of clay minerals is very difficult because of the many different high-temperature reactions which can occur. Secondly, the differentiation is further complicated by the fact that once dehydroxylation has occurred, the remaining disordered structures of all the clay minerals are composed of essentially the same elements (oxygen, silicon, aluminum, magnesium, calcium, potassium, and iron). The manner in which these elements may react within the melt and with the other components presents a wide range of possibilities. For these reasons this research study excluded any attempt to investigate this aspect, especially since a great many other factors are considered. It is emphasized,

however, that a study in this particular area would be worth while and is certainly within the realm of possibility.

3.5.2 Destruction of the Clay-Mineral Structures

The disappearance of the peaks of illite, kaolinite, chlorite, and montmorillonite in the X-ray patterns of all the burned aggregates, R and Z, would indicate that for every burning condition investigated the crystalline clay-mineral structures were destroyed, at least temporarily, even though small amounts of clay minerals may have escaped detection for the reasons enumerated in Section 3.3.2. It cannot be assumed, however, that this destruction will automatically result in durable, strong aggregates, or that rehydration of the clay minerals will not occur. In fact, it is probable that after the first few molecules of hydroxyl water are evolved, the crystalline structure of the clay mineral has undergone enough disruption to modify the characteristic X-ray diffraction peaks. Yet it is under these conditions that some rehydration may take place (5, 9).

This then leads one to expect that other thermal reactions must occur before a permanent dehydrated condition can be assured. Those reactions are the formation of new crystalline phases, formation of a fused, amorphous glass matrix, and reactions between the various mineral components and the glass systems. A discussion of these aspects is therefore included in the following sections.

3.5.3 High Temperature Phases of Aggregates R

The identification of a mineral in the X-ray diffractogram of a mixture cannot be regarded as certain unless its characteristic peaks stand out prominently above the irregularities of the background. Even then, because more than one mineral may yield a reflection from nearly the same interplanar spacing, identification is uncertain unless more than one of the diffraction peaks of the tentatively identified mineral appear at their expected positions.

For these reasons the identification of most of the new crystalline phases formed in the burned aggregates, discussed in the following sections, must be regarded as tentative. Only alpha quartz, whose peaks are prominent throughout all the diffractograms, is present beyond any doubt. Nevertheless, the other minerals, even if uncertainly identified, provide interesting implications concerning the effects of temperature, retention time, and environment within the kiln.

In Figure 3-1 the phase developments of aggregates R can be followed by considering the three different retention times used in the burning process. For aggregates R-2 and R-1 the only new mineral developed is spinel ($MgO \cdot Al_2O_3$ or $FeO \cdot Al_2O_3$), which is generally reported as one of the first transformations to occur when the illite or chlorite is heated in excess of about 1600°F (11). Even though the burning temperature of aggregate R-1 is almost 100°F higher than that of R-2, no additional development has occurred. This indicates that further development of new phases requires higher temperatures and/or longer retention times.

An examination of the patterns for aggregates R-4 and R-3 reveals that several new phases have developed even though the temperatures are lower in both cases.

This emphasizes the importance of retention time in formation of the high temperature minerals. The new minerals are feldspar and α -cristobalite (SiO_2) for R-4 and feldspar and β -quartz (SiO_2) for R-3. The transformation resulting in cristobalite is characteristic of kaolinite and chlorite for temperatures in excess of about 1800°F (5, 11). The absence of cristobalite in aggregate R-3 cannot be explained as it would be an expected component at this higher temperature.

In both patterns R-4 and R-3 peaks at approximately 28° have been labeled as feldspar. Because of the many different forms of feldspar, no specific variety can be named. In addition, although the crystallization of feldspars from a melt at high temperatures is possible (5, 12, 13), this type of phase development is not generally reported with respect to the thermal processing of clay type materials. On the other hand, the transformation of existing feldspars to other crystalline forms has been reported (11). If the feldspar was initially present in raw material R, it is possible that its absence in the raw material pattern was due to its absence in the minus 2-micron fraction on which that pattern was run. Although this latter explanation seems more plausible, no definite conclusions can be made concerning the source of the feldspar in these aggregates.

One other peak on the pattern of R-3 at approximately 26° has been tentatively identified as β -quartz, although the presence of only this one peak limits the preciseness of its identification. The inversion of α -quartz (the common form) to β -quartz at 573°C is rapid and reversible, and even any β -quartz newly formed above 573° would be expected to change to the alpha form on cooling. Only in the case of very rapid cooling would the survival of any β -quartz at ordinary temperatures be considered likely. Nevertheless, Bradley and Grim (14) found β -quartz in the products of firing montmorillonite clays. They suggest that the entrapment of foreign ions (such as Li or Mg) in the β -quartz structure may retard or prevent its return to the alpha form.

The aggregates produced at 48-minute retention times (R-6 and R-5) exhibit a different order of phase development from those last discussed (R-4 and R-3). In this case the generally expected behavior of more extensive transformation at higher temperatures is shown. Here the increase in temperature of 110°F for aggregate R-5 beyond R-6 resulted in the additional development of feldspars, cristobalite and β -quartz. Again, the previous discussions and limitations apply for these minerals. It should also be noted that of these six research-kiln-produced aggregates, the material subjected to the highest temperature for the longest retention time (R-5) exhibits the most extensive transformation behavior.

One other peak not previously discussed for these six patterns is that of hematite (α - Fe_2O_3) in aggregate R-6. Although hematite can result from the transformation of chlorite at approximately 1650°F (11), it can also result from the decomposition and oxidation of non-clay minerals such as pyrite (15). The availability of iron as well as an oxidizing burning condition were both noted in the processing of aggregates R. The particles of aggregate R-6 were particularly notable in that their surfaces were characterized by a relatively thick, rust colored coating, indicative of the presence of iron.

The last pattern of Figure 3-1 is that of the commercially produced aggregate R. This aggregate contains all of the major phases mentioned thus far, and in addition mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). Mullite is reported as a transformation phase for both kaolinite and illite at a temperature as low as 1800°F (5, 11).

When both the number of phases present and their degree of development are considered, it may be concluded that the commercially produced aggregate was most probably subjected to either a higher temperature and/or a longer retention time. On the basis of visits to this particular plant, it would seem that the influence of a longer retention time was responsible for the extensive phase development in this aggregate.

3.5.4 High Temperature Phases of Aggregates Z

The X-ray patterns of aggregates Z (Figure 3-2) will be discussed according to two general unit weight groupings (heavy, Z-2, Z-4 and Z-6, and light, Z-1, Z-3, and Z-5).

The first two aggregates of the heavy group, Z-2 and Z-4, each show three small peaks of anhydrite, CaSO_4 , expectably derived from the gypsum detected qualitatively in raw material Z (Section 3.3.1.1). On the original patterns the most prominent of these peaks can be traced into Z-6 and even into Z-1, but it finally disappears, probably by reaction, at the higher temperatures and longer retention times.

The patterns of aggregates Z-2 and Z-4 generally resemble each other, with the notable exception of a peak tentatively identified as pyrite, FeS_2 , in Z-4. The presence of pyrite is of interest since under the burning conditions employed, its oxidation should begin at approximately 450°C (842°F) (15). However, if a reducing condition exists, pyrite resists decomposition to a temperature of about 630°C (1166°F) (15). In view of this fact, the presence of pyrite in an aggregate burned at 1685°F most probably was the result of nonuniform burning among the different particles as well as throughout the cross sections of the individual particles.

A peak at 29.8° which occurs in Z-2, diminishes in Z-4, and disappears in Z-6 may possibly be due to troilite, FeS , which could result from the dissociation of pyrite. The presence of decomposable sulfides in aggregates Z-2 and Z-4 was evident from the H_2S odor on treatment with hot dilute hydrochloric acid.

Other, smaller peaks in the patterns of Z-2 and Z-4 suggest the possible presence of small amounts of calcite, dolomite and siderite. Raw material Z, and also some lumps of aggregates Z-2 and Z-4, effervesced in cold dilute HCl. Consequently, it seems surprising that calcite peaks are not prominent in the patterns of these two aggregates, unless the carbonate is too fine-grained and poorly crystallized to give good X-ray reflections. As mentioned in Section 3.3.1.2, carbonates were eliminated in the preparation of the raw material sample for X-ray diffraction.

Alpha quartz, feldspar, and spinel appear in the patterns of all three of the heavy aggregates Z.

It is apparent that in kiln runs Z-2 and Z-4 maximum temperatures of approximately 1700°F and retention times of 34 minutes were not sufficient for the complete decomposition of the accessory or extraneous min-

erals contained in the clay. As some of these are not inert materials, the desirability of their decomposition is obvious. Anhydrite can rehydrate to gypsum, with considerable expansion. Under certain conditions dolomite has caused cement-aggregate reactivity (16). Although sulfur in the sulfide form has not been well publicized as harmful to concrete, the reactive nature of its oxidation products, sulfates, has received much attention (17, 18).

Aside from considerations of chemical reactivity, discrete particles of nonclay minerals such as quartz, calcite, dolomite, pyrite, etc., may serve as points of weakness in the aggregate structure. For example, discrete particles within a fused matrix may result in stress concentrations or likely points for crack initiation. These comments are especially applicable to those raw materials in which a concentrated grouping of nonclay minerals occurs along planes of bedding as is often seen in alternating laminae of clay and silt. Unless these minerals are decomposed and/or reacted in some manner so that they become an integral part of the fused structure of the aggregate, their presence is likely to be undesirable.

The change from the heavy to the light aggregate Z represents a relatively large increase in temperature, greater than 150°F. Accompanying this temperature increase was the development of mullite in all three light aggregates (Z-1, Z-3, and Z-5). In fact, the crystalline mineral components of all three of these light aggregates

are the same, α -quartz, feldspar, spinel, cristobalite, and mullite. Of these three aggregates, Z-1 reflects the most significant behavior. The fact that the mullite phase developed at this short retention time, 20 minutes, emphasizes the importance of temperature in the processing of raw material Z. Therefore, for this particular raw material, an increase in retention time above 20 minutes apparently produces no significant change in high-temperature phases as long as the temperature is held between 2010 and 2040°F. This does not imply that other types of thermally induced changes are not occurring (fusion, bloating, etc.).

3.5.5 General Summary of X-ray Analysis

Several useful comments can be made on the basis of the X-ray diffraction studies. First, no clay minerals were detected by the technique used in X-ray analysis of the burned aggregates. Second, the development of high-temperature minerals tends to increase with either or both temperature and retention time, although the parameter showing the greater influence varies with the conditions and with the raw material. Third, with both materials R and Z, the order of new phase development was spinel, cristobalite, mullite. Finally, in the decomposition of possibly detrimental nonclay minerals in material Z, the temperature seemed more effective than the retention time. In this case either 1850°F at 48 minutes or 2010°F at 20 minutes was sufficient for the decomposition of carbonates, sulfides, and most of the sulfates.

IV. Studies Using Differential Thermal Analysis, Effluent Gas Analysis and Gas Chromatography

4.1 General Statement

The use of DTA for the identification of clay minerals in samples containing two or more different mineral species is difficult. Therefore for this purpose X-ray diffraction analysis is the preferred method. However, for the study of the thermal transformations occurring during the heating of clays DTA is an excellent method of approach. With this technique reactions occurring within the samples are indicated by exothermic (heat given off) or endothermic (heat absorbed) behavior throughout a programmed heating cycle. The resulting DTA test patterns give the nature of the reactions, exothermic or endothermic, and the temperature ranges over which they occur.

Although DTA is superior to X-ray diffraction analysis in one respect, that is, reaction temperatures are indicated, many of the individual thermal reactions cannot be directly identified by this technique alone because a great many different reactions yield the same general type of DTA test pattern. All oxidation reactions, such as the oxidation of iron, are exothermic. Decomposition reactions (of carbonates, for example) causing evolution of a gas are endothermic. Many reactions involving merely a shift in atomic structure, such as the alpha-beta quartz inversion at 573°C, are endothermic also. If a reaction involves more than one of these processes the

exothermic and endothermic effects may partially or completely counteract each other.

The development of a gas-detecting unit for use in conjunction with DTA adds a higher degree of sophistication to thermal analysis techniques. This method, EGA, provides data on the temperature range over which a gas is evolved, and thus gives additional information concerning the reaction taking place. It does not provide for the identification of the gas, and thus suffers from a handicap which may limit its usefulness.

If the identification of the evolved gases were possible, then a combination procedure using X-ray diffraction, DTA, and EGA would represent a virtually complete thermal analysis technique for the study of clay-type materials. In order to add the gas-identification capability to the experimental program, a gas sampling system was designed and used in conjunction with a gas chromatograph.

4.2 Differential Thermal Analysis (DTA)

Because of the nature of the testing equipment used, a more detailed DTA pattern could be obtained by the use of the standard DTA sample holder instead of that specifically designed for the DTA-EGA combination. Therefore the decision was made to use the standard

DTA sample holder for the definitive DTA patterns and the DTA-EGA combination accessory equipment for the gas analysis work. The more important information and procedures in the use of the DTA equipment are given below.

Equipment Type—R. L. Stone Co., Austin, Texas.
Recorder-controller model KA-2H.
Furnace assembly model J-2.
Thermocouples—platine 1

Heating Rate—12°C/min.

Heating Atmosphere—static room air

Reference Material—Al₂O₃ (−60 + 140 mesh)

Samples—all samples crushed (−60 + 200 mesh)

Raw—50% sample = 0.12 grams

50% inert = 0.12 grams

Burned—75% sample = 0.18 grams

25% inert = 0.06 grams

Furnace—To minimize variation in the heating process, the same furnace was used for all runs.

Recorder Sensitivity—Varied as shown in figures given in this Chapter (Figures 4-5 through 4-9).

A relatively common problem with all types of DTA equipment is the drift in the recorder zero position which occurs during the sample heating. A drift study was made under the standard run conditions to determine if a correction should be applied to the DTA patterns. An inert material was used as the sample in this case and theoretically should have given a straight baseline for its DTA pattern. The results showed an initial endothermic shift in the baseline followed by a relatively straight-line pattern. Since this endothermic shift occurred at a temperature of less than 100°C and was relatively small, it was decided that a correction was not necessary for the proper interpretation of the sample test patterns.

It should be noted here that no special treatment other than crushing and sieving was given to the preparation of DTA samples. Although certain chemical treatments often precede DTA runs for clay analysis work, the writers felt that a better understanding of the thermal processes occurring during the manufacture of synthetic aggregates could be obtained by analyzing both the raw materials and burned aggregates in their original state.

4.3 DTA-EGA Combination

The testing equipment used for the evolved gas study was basically the same as that described for DTA except that a gas detector unit and a different type of sample holder was required. Information related to the sample preparation and testing is as follows:

Equipment Type—R. L. Stone Co., Austin, Texas
Gas Detector—thermal conductivity
Detector Power Supply—model EGA

Sample Holder—EGA type
Recorder Controller—model KA-2H

Thermocouples—platinum—
platinum-10% rhodium

Heating Rate—12°C/min

Carrier Gas and Reference Gas—oxygen @ 20 cc/min.

Reference Material—Al₂O₃ (−60 + 140 mesh)

Samples—all samples crushed (−60 + 200 mesh)

Raw: 0.24 grams, no inert dilution

Burned: 0.24 grams, no inert dilution

Recorder Sensitivities and Gas Detector Gain—
Varied as shown in this chapter figures.

EGA Bridge Current—135 ma.

Carrier Gas Line Temperature—190°C

Gas Detector Cell Temperature—140°C

As mentioned previously, the evolved gases could be indicated by use of EGA but not identified. Therefore, a method was needed to transfer the evolved gas samples from the exhaust outlet of the gas detector cell to the injection port of a gas chromatograph. Although a direct connection can be made between these two units, their locations made this impossible for this study.

Several transfer methods were tried. A system based on the solidification of the evolved gases by liquid nitrogen was only partly successful. The problem here was that the carrier gas, oxygen, was condensed to a liquid. Therefore, no concentration of evolved gases was possible, and in addition, there was danger of large pressure build-up in any closed container as the temperature of the liquid oxygen was raised.

The transfer technique which was used is shown in Figure 4-1. This system, although very simple, provides an excellent means of collecting the evolved gases. A photograph of this system is shown in Figure 4-2 and an over-all view of the DTA-EGA equipment is given in Figure 4-3.

The flow of gases through the DTA-EGA units can be traced by referring to Figure 4-1. The carrier gas and reference gas flow rates are controlled with the aid of needle valves and a soap bubble flow meter so that both flow at the same rate (20 cc/min.). The reference gas flows directly to a heating chamber and out through the detector cell. The carrier gas flows through the sample in the furnace and out through the heating chamber and detector cell. From the cell, the carrier gas, which now also contains evolved gases, flows through a tee connector to a gas syringe.

This syringe is made of glass and fitted with a threaded plunger rod. In operation the plunger control is slowly turned so that a soap bubble in the flow meter remains stationary. This insures that the entire gas sample is caught in the syringe. The gas transfer is made by removing the rubber tubing at the head of the syringe and capping the syringe with a special fitting used for injection into the gas chromatograph column.

In this study, several syringes were fabricated to make possible the continuous sampling of gases throughout the sample heating range. In general, gas samples

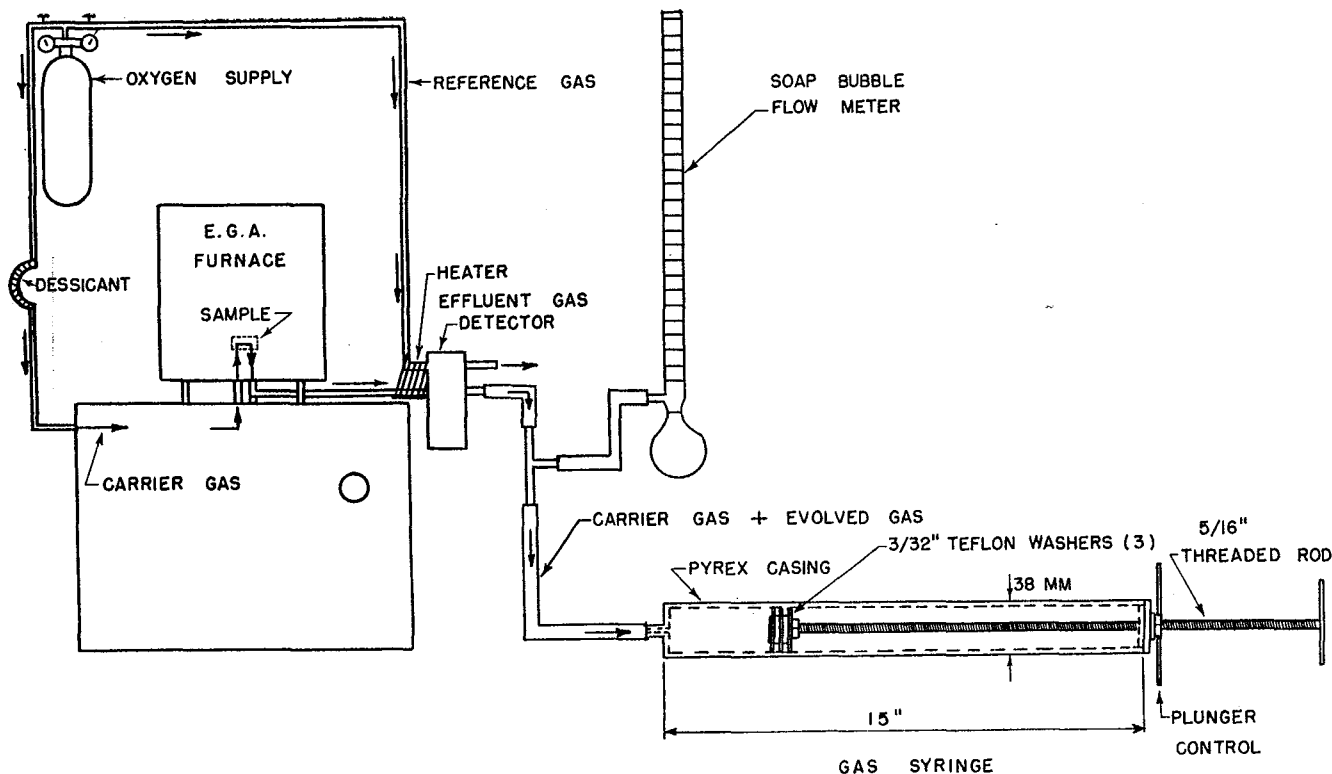


Figure 4-1. DTA-EGA gas sample collection system.

were collected over temperature ranges of 100°C. This required approximately one-half of the volume of each syringe. Since the chromatograph was located in an adjacent room two men were required for this procedure to work effectively.

As with the use of the standard DTA unit, a drift line study was made for DTA-EGA combination equipment. Drift lines were obtained for both the DTA and EGA patterns under standard operating conditions with an inert material used as the sample. These patterns showed a slight instability below 100°C followed by relatively straight lines. This behavior presented no problem in the interpretation of actual test results, and accordingly, no pattern correction was used.

4.4 Gas Chromatography

The identification of the gases evolved in the burning of clay-type materials has previously been studied in considerable detail (19, 20, 21). However, the methods used are either time-consuming chemical procedures requiring a complex arrangement of apparatus or they are very simple techniques which do not provide the information necessary for a thorough and useful understanding of the bloating process.

The collection of useful data on the process of gas evolution under conditions which are realistically related to the actual production of synthetic aggregates requires a continuous analysis of evolved gases throughout the burning cycle. Gas chromatography was the method

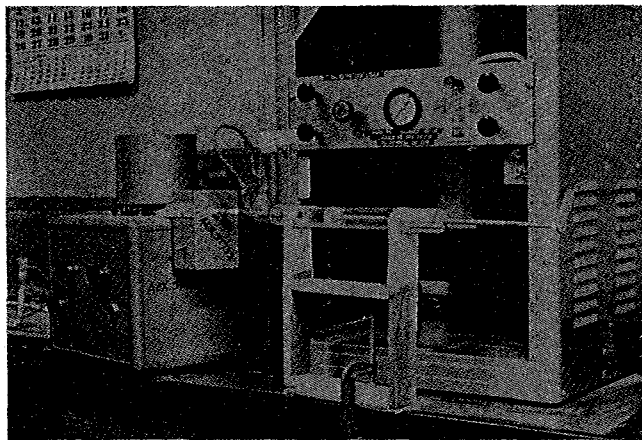


Figure 4-2. DTA-EGA gas sampling technique.

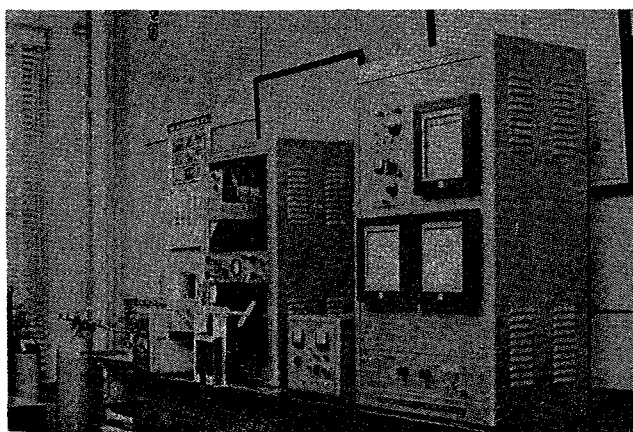


Figure 4-3. Over-all view of DTA-EGA test equipment.

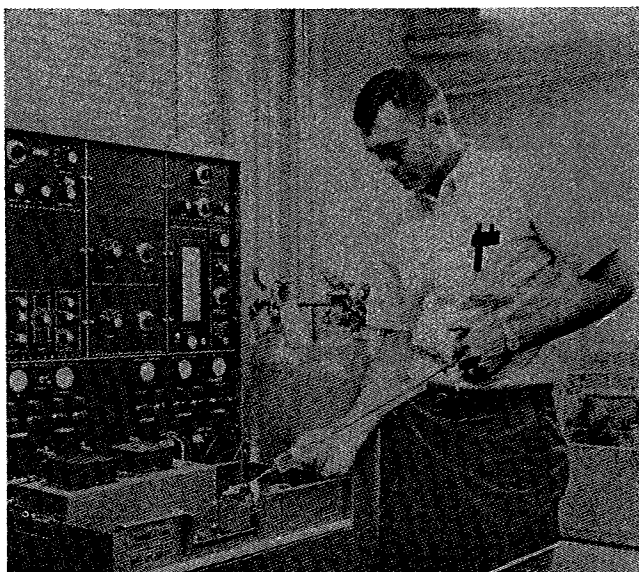


Figure 4-4. Injection of a sample into the column of the gas chromatograph.

chosen for gas identification because of the ease and speed of operation. The equipment and important run parameters are:

Gas Chromatograph Unit—Beckman GC-4

Column-Packing—Porapak Q (80-100 mesh)
Type—6 ft. long, $\frac{1}{8}$ in. O. D. Stainless Steel
Temperature—90°C

Carrier Gas—Helium @ 50 cc/min

Detector—Type—Thermal Conductivity
Temperature—115°C
Current—150 ma

Sample Injection—Pneumatic valve and 0.5 cc sample loop

Probably the most important component of the gas chromatograph is the gas-separating-column packing material. A great many types of packing are available, but their use is generally limited to a small number of specific types of gases. Therefore, the selection of a packing material for use with an unknown number of unknown gases is very difficult. There always exists the possibility that the packing material used is not separating all of the gases in a particular sample.

To partially solve these problems in choosing a column packing material, several manufacturers of chromatograph equipment were contacted for information. As a result, a material developed for the space industry was indicated as suitable for this study. This material, commercially known as Porapak, has been described by Wilhite (22) as being capable of separating sixteen different gases in a single sample. Among these sixteen gases are those commonly reported as products of the firing of clays such as used for the production of synthetic aggregates (23). These gases are H₂O, CO₂, CO, SO₂, O₂, H₂ and H₂S.

In addition to choosing the proper packing material, operating the chromatograph column at the proper temperature is very important, because the column temperature greatly affects the separating ability of the packing

material. Basically the packing material separates the different gases of a sample into groups of like molecules which leave the column at fixed positions within the carrier gas stream. As the molecule groups pass the detector, a signal is recorded with respect to time on a strip chart recorder. If the temperature of a given column is increased, the general result is a more closely bunched grouping and faster travel time through the column. Therefore, each column packing must be calibrated under various conditions to determine the proper temperature and carrier gas flow rate settings.

In order to use the gas chromatograph for quantitative gas analysis, it was necessary to calibrate the column for each type of gas indicated. This was accomplished by injecting gases of known type and concentration into the column and measuring the height of the peaks shown on the recorder traces. After a number of different concentrations of a given gas were injected, a curve was prepared for use in determining the quantities of gas present in actual sample runs. A view of the gas chromatograph showing the injection of a gas sample is given in Fig. 4-4.

4.5 Interpretation of DTA Patterns

4.5.1 DTA Analysis of Raw Material R

The DTA patterns for raw material R and all of the burned aggregates R are shown in Figure 4-5. The uppermost pattern gives the thermal behavior of the raw material as indicated by endothermic reactions (below the base line) and exothermic reactions (above the base line).

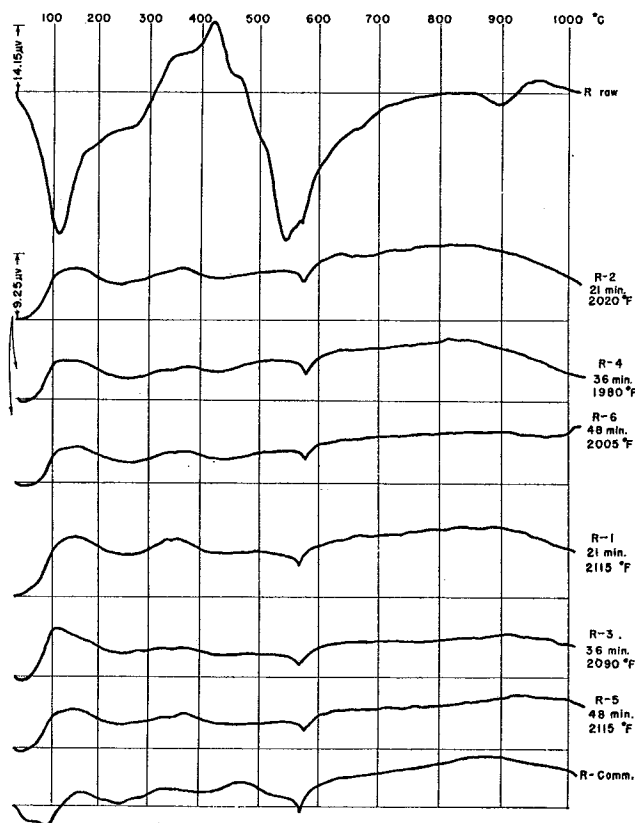


Figure 4-5. DTA patterns for raw and burned aggregate R.

In the pattern of the raw material, a number of endothermic reactions are indicated by downward peaks at about 110°C, 540°C, 570°C, and 900°C. In addition, a slight endothermic hip is shown at about 260°C. In general these endothermic reactions are indicative of the clay mineral composition previously identified (Section 3.5.1 and Figure 3-1) as kaolinite, illite, and chlorite. The 110°C peak represents the loss of adsorbed water, the 540°C peak signifies the major dehydroxylation of the clays, and the 900°C peak represents the final disruption of the dehydrated clay structures (11). The small sharp peak at about 570°C corresponds to the alpha-beta quartz inversion. The slight endothermic hip at about 260°C has not been definitely identified, but could result from the dehydration of nonclay minerals such as ferric and aluminum hydrates (11).

Raw material R shows two exothermic peaks. The first is a nonsymmetrical exotherm occurring between 300 and 450°C and is probably indicative of the oxidation of organic matter (24). The second exotherm is shown at about 950°C and represents the formation of high temperature mineral phases such as spinel, cristobalite and mullite (24).

4.5.2 DTA Analysis of Burned Aggregates R

By comparison, the seven DTA patterns for the burned aggregates R show almost identical thermal behavior although very different from that of the raw material. First, the initial exothermic behavior shown by all but the commercial aggregate R is difficult to explain. Separate studies show that it is not due entirely to base-line drift. It may be caused by a difference in heat conduction between the sample and the reference material in the furnace.

The more significant thermal characteristics of these seven patterns are the slight exothermic nodes between about 300 and 500°C, the absence of the clay dehydroxylation peaks, and the absence of any high-temperature activity between 900 and 1000°C. The rather broad exotherms in the 300-500°C range represent the continued oxidation of the substances responsible for more pronounced exotherms in the raw material R. The disappearance of the large dehydroxylation peak at about 540°C indicates that the clay minerals have been dehydrated in all the aggregates, and the absence of activity at about 900°C indicates that the disrupted clay structures have already reacted to form high-temperature minerals during the initial rotary kiln processing. In all the aggregates the sharp endotherms at about 570°C correspond to the alpha-beta quartz inversion.

Thus, on the basis of DTA data alone, it appears that the various processing conditions used for the production of aggregates R resulted in the same relative degree of transformation of the raw material.

4.5.3 DTA Analysis of Raw Material Z

The DTA patterns for the raw and burned material Z are shown in Figure 4-6. The upper pattern of Figure 4-6 is that of the raw material and shows a relatively high degree of thermal reactivity. For this reason, an accurate identification of the mineral components is difficult. However, a rather broad interpretation of the peaks can be given.

As the temperature of raw material Z is raised, the loss of adsorbed water occurs as shown by the large

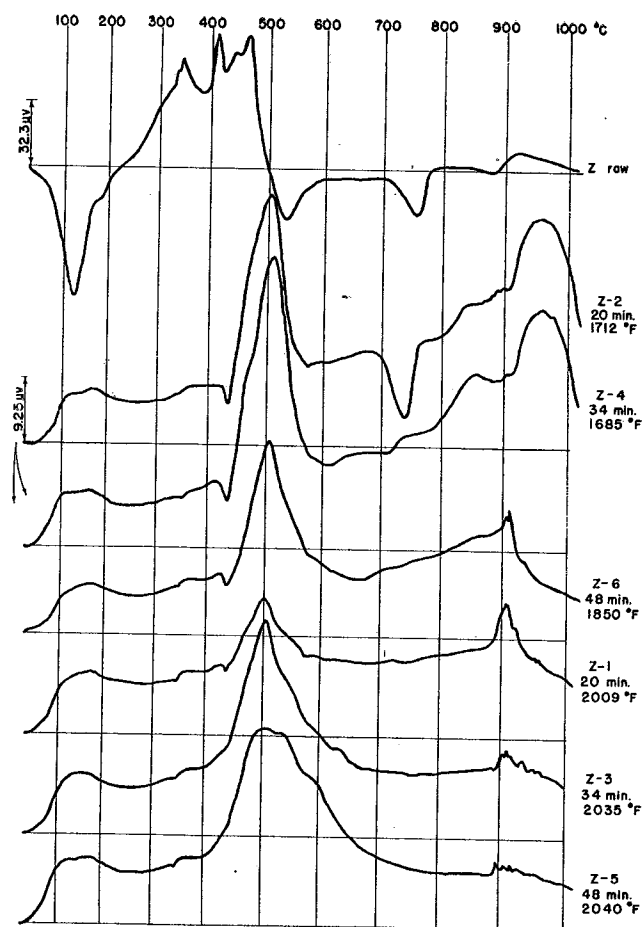


Figure 4-6. DTA patterns for raw and burned aggregate Z.

endothermic peak at about 120°C. This peak is followed by a slight endothermic hip at about 190°C which perhaps reflects the presence of montmorillonite (11) or of some nonclay mineral such as gypsum (25). The presence of montmorillonite as well as kaolinite and illite has been confirmed by X-ray analysis as mentioned earlier. Between approximately 250 and 500°C, an intense exothermic reactivity is shown. The jagged nature of these peaks suggests that they are the result of the oxidation of several components, probably organic matter, pyrite or marcasite, (11, 15, 24) and perhaps others.

Because of the extensive exothermic activity just prior to the endothermic peak at 540°C, it is difficult to determine the point of initiation of the endotherm. However, a glance at the patterns for aggregates Z-2, Z-4, and Z-6 seems to indicate that this endotherm has its origin at approximately 420°C and is then rapidly obscured by an exothermic reaction. This particular endotherm probably represents the dehydroxylation of all three clay minerals, although the influence of a montmorillonite endotherm is not certain. This is because the dehydroxylation peak for montmorillonite may occur at any position within a relatively large temperature range, depending upon the chemical composition of the mineral (5, 9, 11).

Because of the variable nature of montmorillonite, the endotherm at about 760°C could be attributed to it.

But more probably this peak was caused by the decomposition of carbonates, or by their reaction with the clay. The presence of considerable carbonate in raw material Z was indicated by preliminary tests, and also by gas analysis as described in the following section.

The final reaction of raw material Z is indicated by the endothermic-exothermic inversion at about 900°C. This is similar to the high temperature reaction discussed for raw material R and can be attributed to the final disruption of the dehydrated clay structures and the development of high temperature minerals such as spinel, cristobalite, and mullite.

4.5.4 DTA Analysis of Burned Aggregates Z

In an examination of the DTA patterns for burned aggregates Z, several significant reactions are noted. First, all three of the heavy weight aggregates (Z-2, Z-4, and Z-6) show what appears to be the initial portion of a dehydroxylation endotherm at about 430°C, which is immediately obscured by a large exothermic reaction. To a lesser extent aggregate Z-1 shows this same behavior. Although no confirmation from X-ray analysis was obtained, this endotherm suggests that some clay mineral may still be present in these low-temperature aggregates, perhaps in a partially dehydrated and disordered form. That the endotherm is caused by loss of water is shown by EGA analysis (Section 4.6.5 and Figure 4-9).

The large exotherm common to all the burned aggregate patterns represents the continuation of the oxidation reactions indicated in the raw material for this temperature range. The apparent shift of this peak to a slightly higher temperature (500°C) suggests that some of the more easily oxidizable constituents have been removed in the kiln. Although the relative sizes of these exotherms are possibly related to the amounts of oxidizable materials remaining in the aggregates, no conclusive statement can be made to this effect.

The next point of interest in the burned aggregate patterns is the large endothermic peak at about 740°C for Z-2. The similar peak in the pattern of the raw material was attributed to the loss of carbon dioxide from carbonates, some of which evidently escaped decomposition in the kiln processing of aggregate Z-2. The presence of this peak classifies aggregate Z-2 as the least thermally transformed of all the burned aggregates Z.

A final point of interest concerning the DTA patterns is related to the high temperature endotherm-exotherm inversions. Note that the two aggregates, Z-2 and Z-4, which were subjected to the least extensive thermal processing, are characterized by very large exotherms between 900 and 1000°C. On the other hand, the remaining four aggregates, processed under more extensive burning conditions, show considerably less reactivity in this temperature range. It may be concluded that these high temperature exotherms are caused by the formation of the high temperature minerals as indicated by the pattern for the raw material. Apparently, aggregates Z-2 and Z-4 had not been adequately processed in the rotary kiln for this reaction to have taken place. As a result, this reaction was carried to completion by a second heating in the DTA furnace.

By comparison, note that the high temperature reactivity of the last four aggregates not only is less

extensive but also shows a direct relationship to the burning conditions. As the retention time and temperature are increased, the size of the resulting exotherm is decreased. Note that for the highest temperature and the longest retention time the high temperature exotherm has almost disappeared. This condition most closely approximates that shown by all of the burned aggregates R.

In an attempt to determine the phase changes responsible for the differences in high temperature exothermic behavior of aggregates Z, X-ray diffraction analysis was employed. From Figure 3-2, it appears that the formation of cristobalite corresponds to the decrease in the magnitude of the exotherms of Z-6, Z-1, Z-3, and Z-5. If this assumption is correct, then the smaller exotherms of these last four aggregates probably represent the continuation of the cristobalite-forming reactions initiated during rotary kiln processing.

4.6 Interpretation of EGA and Gas-Chromatograph Data

4.6.1 General Statement

The data for the evolved gas analysis are presented in the form of a DTA pattern with an evolved gas pattern superimposed on it. Figure 4-7 shows these patterns for raw materials R and Z. A few comments are helpful in interpreting the results. First, the DTA patterns (solid lines) are obtained by the same general technique as that used in the standard DTA analysis discussed in the previous section, but, because of the nature of the

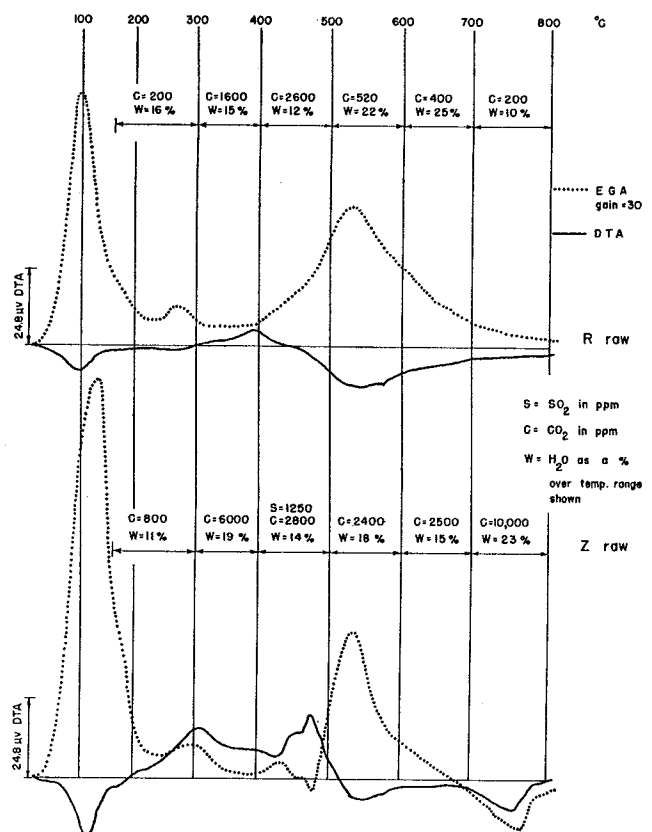


Figure 4-7. DTA and EGA patterns of the raw materials, including gas determinations by gas chromatography.

equipment used, they are characterized by less sensitivity in general. In addition, note that because of the danger of oxidation of metal parts, a limit of 800°C was used in all EGA runs.

The EGA patterns are indicated by dotted lines superimposed on the DTA patterns. In all of the EGA patterns the evolution of a gas is signified by the deviation of these dotted lines from the horizontal. During the course of the preliminary calibration work, it was noted that the evolution of H₂O caused an upward deflection in the pattern while CO₂ caused downward deflections.

The quantitative gas data obtained by the use of the gas chromatograph are shown above the patterns of Figure 4-7. For CO₂ and SO₂ the quantities are expressed as parts per million (ppm) of the effluent sample given off over the specific temperature ranges shown. For H₂O the quantity evolved is expressed as the percent of the total water evolved over the temperature range of 150 to 800°C. This treatment of the data for water was required because of the difficulty encountered in calibration as parts per million.

4.6.2 Raw Material R

The DTA-EGA patterns for raw material R are shown in the upper portion of Figure 4-7. According to the EGA pattern, the endothermic peaks at 100°C, 260°C, and 530°C all represent the evolution of water. This agrees with the previous DTA analysis of this material and reinforces the assumption that the slight endothermic hip at about 260°C in Figure 4-5 is caused by a dehydration reaction.

The gas chromatograph reveals a considerable evolution of CO₂ between 300 and 400°C, and even more between 400 and 500°C. This indicates that, as previously surmised, the large exotherm in this temperature range in Figure 4-5 is primarily the result of the oxidation of organic matter. It is interesting that the water produced by the same reaction very nearly counteracts the EGA effect of the CO₂, so that the EGA curve remains practically horizontal. But with further rise in temperature the dehydroxylation of the clay minerals begins as the combustion of the organic matter approaches completion, and the resulting excess of evolved water causes the EGA curve to rise steeply to a peak at about 540°C, corresponding to the endothermic peak of Figure 4-5. It is notable that the dehydroxylation reaction is not nearly so abrupt as has been implied by some authors. In this particular case it is spread over a temperature range of 300°C. This fact points to the need of adequate time as well as sufficiently high temperatures for the complete dehydroxylation of the clay minerals.

A final comment concerning the processing of aggregate R is that apparently the gases producing the bloated structure are a combination of CO₂ and H₂O. It may also be significant that the uniformly small size and distribution of the pore structure of aggregates R is possibly due to the very gradual evolution of the bloating gases as seems to be indicated at the higher temperatures of the EGA pattern.

4.6.3 Raw Material Z

The lower pattern of Figure 4-7 is that of raw material Z, and, as might be expected, it shows consid-

erably more reactivity than that of raw material R. First, there is a large quantity of adsorbed water driven off at about 120°C. Also, the slight bulge in the EGA pattern at about 180°C corresponds to the endothermic hip in the DTA patterns of Figures 4-6 and 4-7. This was previously attributed to the dehydration of some mineral such as montmorillonite or gypsum.

From about 250 to 300°C the effect of the evolution of water on the EGA curve overcomes that of the CO₂ resulting from the combustion of the organic matter, but between 300 and 400 degrees the reverse is the case. At a little over 400° water again predominates, but its EGA effect is quickly counteracted by a strongly exothermic evolution of other gases, culminating in a peak at about 470° which the chromatograph suggests is due to the evolution of SO₂, probably from the oxidation of pyrite or marcasite. After oxidation decreases, dehydroxylation of the clay minerals proceeds to a maximum rate at about 540°C, as in raw material R.

The final reaction indicated by this pattern of raw material Z occurs at about 750°C and is characterized by an endothermic DTA peak and a downward EGA peak. This evidence and the chromatograph data indicate the evolution of much CO₂ gas, almost certainly from the decomposition of the carbonates present. However, a rather large water content for the gases evolved in this temperature range is indicated by the chromatograph data. Possibly still another dehydroxylation reaction is taking place, but there is no other evidence to support such a conclusion.

The principal gases causing the bloating of aggregates Z appear to be H₂O and CO₂, as was the case with aggregates R. However, the role of SO₂ as an additional bloating gas in this case seems certain because the odor of SO₂ was detected coming from several of the shorter retention time aggregates after their discharge from the rotary kiln.

4.6.4 Burned Aggregates R

The DTA-EGA patterns for all of the burned aggregates R are shown in Figure 4-8. However, in this figure the evolved gas concentrations are not shown as parts per million, but as percentages of the gas evolved through the same temperature range during the heating of the raw materials. In other words, the chromatograph data shown essentially represent the amounts of unreacted gas-producing substances remaining in the aggregates after processing in the rotary kiln. Because the total volume of the gas samples changed slightly, the percentages given are only approximate. Quantitative determination of the water was not possible because of its adsorption on the apparatus at the low concentrations involved.

In Figure 4-8 all the burned aggregates show very similar characteristics. The initial evolution of gas at about 100°C represents adsorbed water. The associated exothermic reaction indicated by the DTA pattern is unexplained, but as previously suggested could be caused either by baseline drift or by differences in heat conduction in the apparatus.

Apart from the alpha-beta quartz inversion at 570°C, the only other activity of these aggregates shown in Figure 4-8 is the evolution of CO₂ detected by the gas chromatograph in the temperature range of 300-500°C.

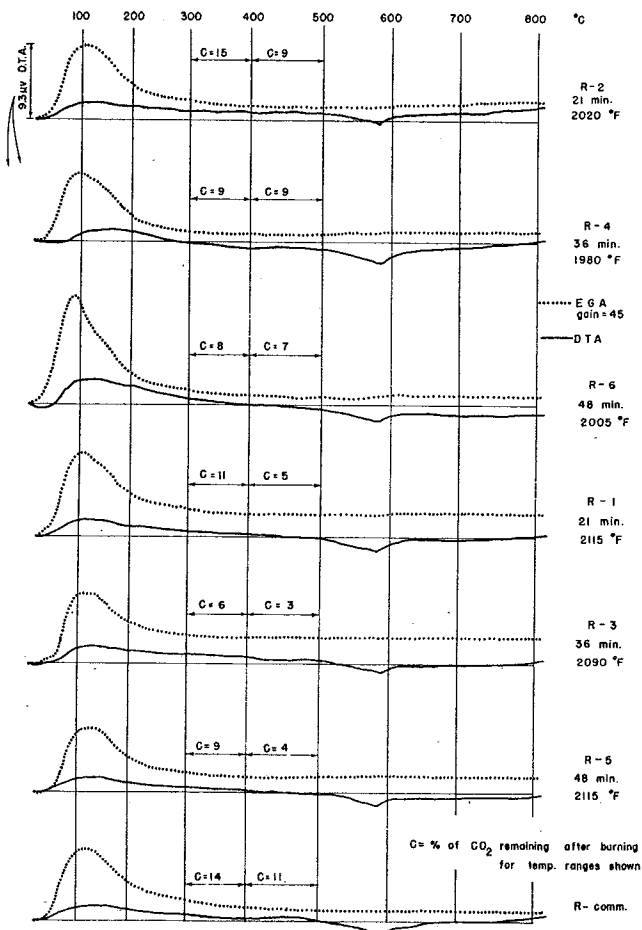


Figure 4-8. DTA and EGA patterns for burned aggregates R with gas chromatograph data on evolved gases.

The source of this gas is apparently the continued oxidation of organic matter not reacted during the rotary kiln processing. The counteracting effect of the simultaneous evolution of water may be the reason for the absence of any peak on the EGA trace. The thermal changes involved apparently are too small to be detected by the DTA-EGA arrangement, but the more sensitive DTA analysis of Figure 4-5 does show slight exothermic reactions for all of the aggregates at these temperatures.

Several important points can be made on the basis of this behavior. First, even though X-ray analysis indicated that the commercial aggregate R was the most extensively processed material of this group, it contains a comparatively larger content of unburned carbon. However, this is understandable when one considers that the commercial aggregate was produced under less oxidizing burning conditions than those of the research kiln aggregates.* Second, it is interesting to note that although the measured temperature of the aggregates in the kiln was much higher than that initiating the reaction in question, the kiln-produced reactions were not carried to completion. This again emphasizes that although the true reaction temperatures are given by

*Based on personal observations and the darker color of the commercial aggregates.

such tests as DTA, similar reactions occurring within the aggregates during actual production runs require specific atmospheres and elevated temperatures for extended periods of time. The most efficient selection of these burning conditions must, of course, be determined for each type of raw material.

4.6.5 Burned Aggregates Z

The EGA-DTA patterns for the burned aggregates Z are shown in Figure 4-9. All of these patterns show a typical loss of water at about 100°C as was the case with aggregates R. However, beyond this temperature, considerable differences are shown. First, note that the first three aggregates (Z-2, Z-4, and Z-6) show an endothermic reaction accompanied by an evolution of H₂O at about 410°C. The unconfirmed presence of these endotherms was previously indicated by the DTA patterns of Figure 4-6. It now seems logical to conclude that these endotherms represent the presence of some clay mineral in a state of partial dehydration. Note also in Figure 4-9 that the magnitudes of both the EGA and DTA peaks for this reaction are directly related to the extent of processing of these three aggregates. On the other hand, this particular reaction is essentially missing in the three lighter weight aggregate patterns (Z-1, Z-3, and Z-5), indicating that their increased processing temperatures were effective in destroying the clay minerals.

The exotherms shown by all of these burned aggregates in the temperature range of 400°C to 600°C are

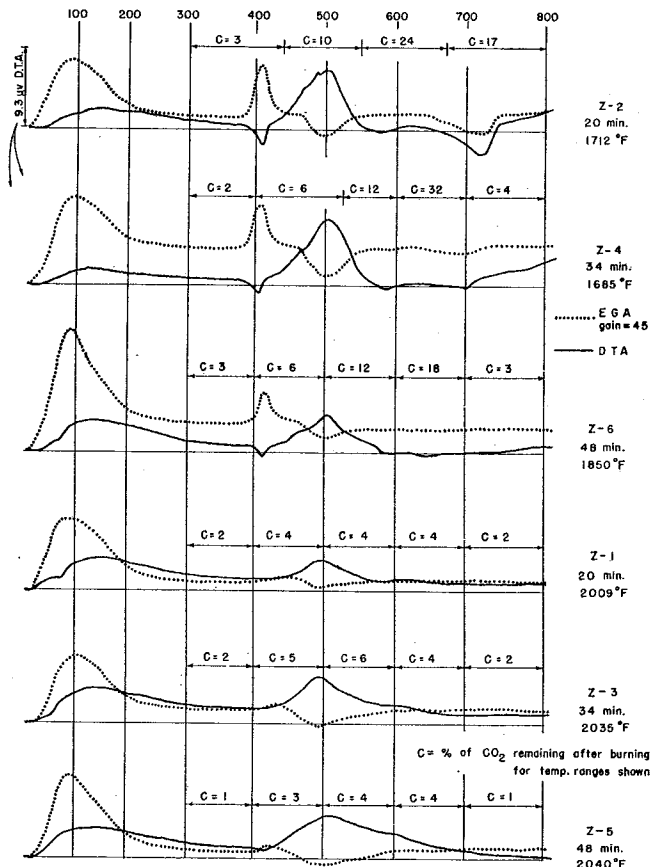


Figure 4-9. DTA and EGA patterns for burned aggregates Z with gas chromatograph data on evolved gases.

synonymous with those shown by the DTA patterns of Figure 4-6. The corresponding EGA patterns as well as the chromatograph data confirm that these peaks are associated with the oxidation of organic matter. Here again, the CO₂ concentrations given by the chromatograph data show a direct relationship to the extent of thermal processing.

At approximately 720°C, aggregate Z-2 is characterized by an endothermic reaction and a downward EGA peak. The chromatograph data and shape of the EGA peak indicate that this peak represents the decomposition of a carbonate. A similar conclusion was indicated by the results of the standard DTA study (Figure 4-6).

The DTA and EGA patterns for aggregate Z-4 show a very slight indication of a reaction at 700°C. The CO₂ data for the 600° to 700° temperature range indicate that this reaction was also caused by the decomposition of a carbonate. The remaining four aggregates show no noticeable endothermic reaction in this temperature range, indicating complete elimination of the carbonate, although a little CO₂ is still being evolved from the slow oxidation of the organic matter.

In conclusion, the results of the evolved gas analysis are seen to be very useful in determining the degree of transformation which has occurred during aggregate processing. Based on the data of Figure 4-9, it can be concluded that aggregates Z-2, Z-4, and Z-6 were not processed as thoroughly as Z-1, Z-3, and Z-5. In addition, the order of increased processing as indicated by the temperature and retention times shows a direct relationship to the thermal reactivity as shown by Figure 4-9.

4.7 General Summary of the Transformation Study Results

4.7.1 Comment on the Method.

The techniques of X-ray diffraction, DTA, EGA, and gas chromatography supplement each other so that a fairly complete thermal transformation study can be made on either raw materials or burned aggregates. The versatility of this combination technique is emphasized by the following list of transformation-related factors which can be studied by this method.

1. Detection of the presence or absence of crystalline minerals, including clay minerals.
2. Detection of endothermic and exothermic reactions and temperatures at which they occur.
3. Detection of gas-producing reactions and temperatures at which they occur.
4. Identification of evolved gases.
5. Quantity determination of evolved gases.
6. Determination of the extent to which high temperature transformations have occurred.

4.7.2 Summary of Results

The results presented in this section represent the conclusions reached from an analysis of all the data of the transformation study. For both raw materials and all burned aggregates, a short statement is given which identifies the important components in each particular material.

R raw	clay minerals—chlorite (7%), illite (62%), kaolinite (31%) other components— α -quartz, organic matter, trace of calcium carbonate and gypsum bloating gases—EGA indicates gradual release of H ₂ O and CO ₂
R-2 21 min. 2020°F	X-ray—no clay minerals detected; spinel, α -quartz present DTA, EGA, GC*—no high temperature phase transition detected in DTA burn, slight indication of the presence of organic matter
R-4 36 min. 1980°F	X-ray—no clay minerals detected; spinel, α -quartz, α -cristobalite, feldspar present DTA, EGA, GC—same as R-2
R-6 48 min. 2005°F	X-ray—no clay minerals detected; spinel, α -quartz, hematite present DTA, EGA, GC—same as R-2
R-1 21 min. 2115°F	X-ray—no clay minerals detected; spinel, α -quartz present DTA, EGA, GC—same as R-2
R-3 36 min. 2090°F	X-ray—no clay minerals detected; spinel, α -quartz, β -quartz, feldspar present DTA, EGA, GC—same as R-2
R-5 48 min. 2115°F	X-ray—no clay minerals detected; spinel, cristobalite, α -quartz, β -quartz, feldspar present DTA, EGA, GC—same as R-2
R-comm.	X-ray—no clay minerals detected; spinel, cristobalite, mullite, feldspar, α -quartz present DTA, EGA, GC—slightly more organic matter than other six aggregates R
Z-raw	clay minerals—montmorillonite (29%), illite (44%), kaolinite (27%) other components— α -quartz, pyrite, organic matter, much calcium carbonate, small amount of gypsum bloating gases—EGA indicates large quantities and rapid evolutions of CO ₂ , SO ₂ , and H ₂ O
Z-2 20 min. 1712°F	X-ray—no clay minerals detected; spinel, anhydrite, α -quartz, feldspar present DTA, EGA, GC—incomplete formation of high temperature phases, probable presence of partially dehydrated clay minerals, sizeable quantity of organic matter, and carbonate.

*GC—gas chromatography.

Z-4 *X-ray*—no clay minerals detected; spinel, pyrite, anhydrite, α -quartz, feldspar present
34 min.
1685°F

DTA, EGA, GC—incomplete formation of high temperature phases, probable presence of partially dehydrated clay minerals, sizeable amount of organic matter, slight indication of carbonate

Z-6 *X-ray*—no clay minerals detected; spinel, cristobalite, α -quartz, feldspar present
48 min.
1850°F

DTA, EGA, GC—slight indication of incomplete high temperature transformation, slight indication of partially dehydrated clay minerals, appreciable organic matter

Z-1 *X-ray*—no clay minerals detected; spinel, cristobalite, mullite, α -quartz, feldspar present
20 min.
2009°F

DTA, EGA, GC—small amount of organic matter, slight indication of incomplete high temperature transformations

Z-3 *X-ray*—no clay minerals detected; spinel, cristobalite, mullite, α -quartz, feldspar present
34 min.
2035°F

DTA, EGA, GC—small amount of organic matter, very slight indication of incomplete high temperature transformations

Z-5 *X-ray*—no clay minerals detected; spinel, cristobalite, mullite, α -quartz, feldspar present
48 min.
2040°F

DTA, EGA, GC—small amount of organic matter, very slight indication of incomplete high temperature transformations

4.8 Implementation Statement

The research reported herein summarizes results on fundamental properties of synthetic aggregate, using analytical evaluation techniques. While the research was valuable and necessary to understand the transformation phenomena associated in the production of synthetic aggregates, no direct implementation within the Highway Department is recommended. It is recommended that these techniques continue to be used in appropriate research programs in order to aid in the development of suitable engineering analysis techniques.

The above statement represents the combined opinions of the study contact representative and the authors and should not be construed as departmental policy.

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