Methodology for Improvement of Oxide Residue Models for Estimation of Aggregate Performance Using Stoichiometric Analysis

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A methodology is presented for improving the predictive ability of oxide-based chemical models that predict aggregate material properties using the chemical composition of the coarse aggregate. Because portland cement concrete is composed of 70 to 85 percent coarse and fine aggregates (by weight), the aggregate material properties have a profound effect on the material properties of the finished concrete and ultimately on pavement performance. An existing computer program, CHEM1, has been used to estimate these concrete properties (compressive and tensile strength, elastic modulus, and drying shrinkage) through stochastic models based on user-input oxide residues. This approach, although adequate for some applications, suffers from the fact that concrete properties are influenced more by the mineralogy of the aggregate than by the oxides formed from their decomposition. Using stoichiometric analysis, the CHEM2 program backcalculates the original mineral composition from the oxides and thereby improves the accuracy of the models. The CHEM2 program also adds the ability to predict for aggregate blends and a model for thermal coefficient of expansion, both of which were lacking in CHEM1.

In Texas Department of Transportation Project 422/1244, concrete specimens were cast from eight coarse aggregate sources commonly used in Texas rigid pavements. Water-cement ratio, other mix design elements, and curing conditions were held as constant as possible so that any variation in concrete properties would be due to the influence of coarse aggregate. The specimens were then tested for tensile strength (f_t), compressive strength (f_c), elastic modulus (E), drying shrinkage (Z), and thermal coefficient (a) after various lengths of curing. Subsequent analysis based on this testing developed descriptive models (based on curing time and aggregate type) and predictive models (based on curing time and chemical composition) (1). This effort was termed the Phase II experiment. Complete mix designs can be found elsewhere (1).

In order to easily apply the chemical models, a computer program, CHEM1, was developed for the IBM personal computer (1). Earlier testing focused only on limestone and river gravel aggregates was termed Phase I (2). This program requires as input the percentage by weight of certain oxide residues produced by standard fusion testing. It then predicts f_t, f_c, E, and Z for curing times ranging from 1 to 28 (256 for Z) days. The object of the program was to give a rough prediction of material properties for concrete made with a new aggregate source before actual laboratory testing.

The overall purpose of predicting concrete material properties for various aggregates is to determine design parameters (steel percent, bar size, etc.) needed to attain a desired level of pavement performance. Using design tools such as the continuously reinforced concrete pavement programs (3), these factors can be estimated. In this way, it is hoped that equal and adequate performance from very different aggregates can be obtained.

CHEM2 OBJECTIVES

Improved Models for Limestones and River Gravels

CHEM1 currently uses one model to predict for all types of aggregates. CHEM2 obtains better results by first identifying the type of aggregate and then making a prediction using a model specifically developed for that aggregate class. This is especially important for aggregate types that produce similar oxide residues [e.g., siliceous river gravel (SRG) and granite, both high in SiO_2] but differ in mineral composition and therefore exhibit characteristic differences when cast in concrete. The program can either identify the class of aggregate by direct user input or determine it through a simple set of IF statements based on the oxide test results. Once the class is determined, the original mineral content is first backcalculated from the oxide residue stoichiometrically (4).

Since limestones and river gravels are the focus of the overall study, special attention has been given to these aggregates. Two new limestones and two new river gravels are currently being tested (Phase II experiment), which will add enough additional data to make more type-specific models possible. These models would estimate differences in strength, modulus, shrinkage, and expansion based on small differences in the characteristic minerals composing the aggregates, presumably calcium carbonate (Ca_2CO_3) and dolomite ($CaMg(CO_3)_2$) for limestone and quartz (SiO_2) for river gravel.

At this time, CHEM2 predictions for aggregates other than limestone or river gravel consist simply of identifying the aggregate (e.g., granite) and producing the absolute or normalized curing curves determined in Phase II.

Prediction of Thermal Coefficient

CHEM1 does not predict thermal coefficient of expansion. This is a vitally important property, particularly for pavements placed in the summer season when temperature extremes are great and

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peak ambient temperature may coincide with peak heat of hydration (as in morning placements). Under such conditions, for a given steel design, a high thermal coefficient tends to produce more closely spaced early-age cracking compared with an aggregate that has a lower coefficient.

Despite the desirability of such a model, problems with using the oxide residues directly prevented the development of a definitive model. This difficulty has been overcome by first backcalculating the original mineral content. Additional thermal coefficient testing in the Phase III experiment will provide additional data to further improve the thermal coefficient model. CHEM2 currently predicts thermal coefficient based on the Phase II data.

Predictions for Aggregate Blends

CHEM2 also adds a facility for predicting the performance of blended aggregates. Phase III testing included an experiment to determine the effect of blending limestone with river gravel at various proportions. This experiment was designed to reveal the shape of the blending curves (Figure 1), which could then be normalized for each material property and used to predict the performance of blends. Initially, it was not known whether the properties of a blended aggregate could be described by the weighted average for the two aggregates (Figure 1, Curve A, linear) or by a nonlinear combination (Figure 1, Curves B and C). Initial results from Phase III testing support Curve A, the simple linear combination. CHEM2 will determine properties for blended aggregates by estimating for each individual aggregate and then taking a weighted average according to the blending ratio.

PROGRAM FLOW

The CHEM2 program operates as follows:

1. User input of chemical composition data is obtained;
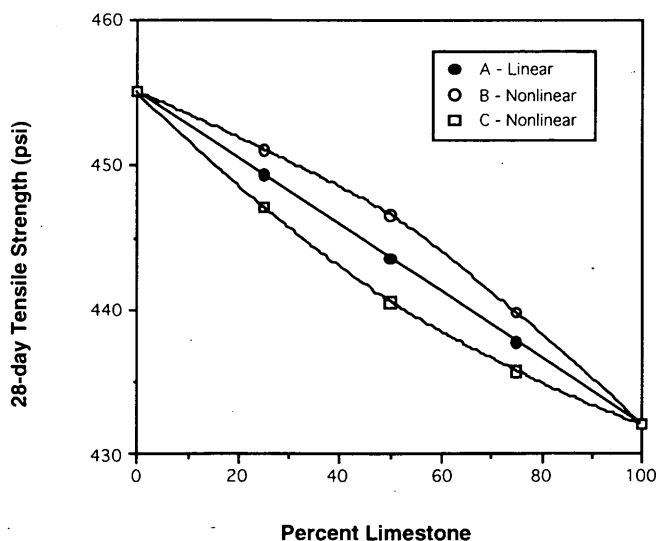2. Prediction models for the five material properties are produced;

FIGURE 1   Possible performance shapes for blended river gravel.
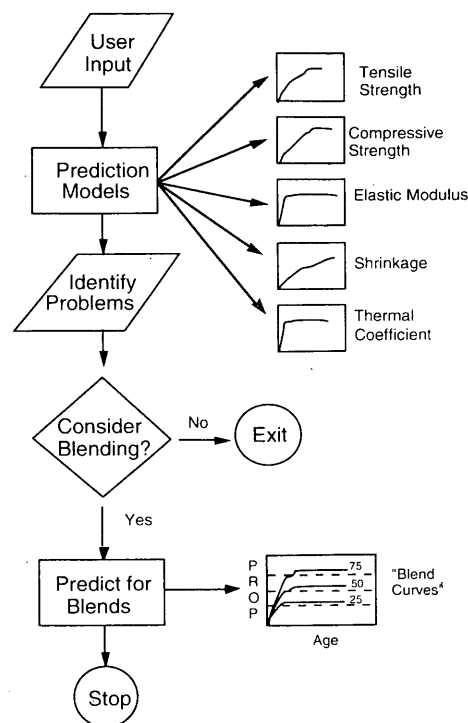

FIGURE 2   CHEM2 program flow.

3. Potential problem areas are highlighted (e.g., excessively high thermal coefficient); and

4. At the user's option, a parametric series of curves is produced predicting the performance of the original aggregate blended 75/25, 50/50, and 25/75 with a standard or user-input limestone (Figure 2). These graphs (Figure 3) have grid lines so that the user can screen print them and determine the approximate blending level needed to produce the material properties that result in the desired level of performance.

STOICHIOMETRIC ANALYSIS

One of the problems encountered in the development of the CHEM1 models was that only the oxide residues were considered as predictors. Since different minerals may break down to different oxides of the same compound (e.g., dolomite and calcite both contribute to the calcium oxide residue), direct empirical modeling based on oxide residue is problematic. Therefore, a methodology was developed for backcalculating the percentage by weight of the various minerals that compose the aggregates used in the Phase II study. Mineral composition determined in this way can then be used to develop more robust predictive models for such aggregate-dependent concrete properties as tensile strength, compressive strength, elastic modulus, drying shrinkage, and thermal coefficient of expansion.

Problems with Existing Chemical Models

Phase II testing under this project collected aggregate chemical composition data for eight aggregates commonly used in Texas

pavements and for a number of additional aggregates (*1*). Several analytical procedures were performed, including determination of principal mineral composition by x-ray diffraction and oxide residue analysis after fusion.

Dossey and McCullough (*1*) document an effort to predict aggregate performance based solely on oxide residues. Although some useful models were developed, some of the models were later determined to have weak predictive ability outside the inference space of the eight tested aggregates. The problem with oxide-based models is that few of the oxides measured actually existed in the aggregate before chemical testing; in fact, most of the oxides were formed by the breakdown of more complex minerals in the sample. For example, little if any calcium oxide (CaO) was present in the aggregate before fusion; most was produced by the oxidation of calcite (limestone, $CaCO_3$), and an additional amount came from dolomite ($CaMg(CO_3)_2$).

This situation gives rise to a fundamental problem: since the amount of each oxide is proportional not to a single mineral but to several, no strong direct correlation is observed between oxide percentage and concrete material properties. The models developed by Dossey and McCullough (*1*) attempt to compensate by considering interactions. These interactions serve as surrogate variables or indirect indicators for the original mineral content of the sample.

Methodology

A much better method is to develop models based directly on the original mineral composition of the aggregates. Fortunately, stoichiometric analysis can be used to backcalculate these percentages (*3*).

Using the results from x-ray crystallography (Table 1), the principal minerals in each sample were determined. Most are composed primarily of any or all of the following: calcite ($CaCO_3$), quartz (SiO_2), or dolomite ($CaMg(CO_3)_2$). A notable exception is Scotland Granite, which contains a substantial amount of the sodium feldspar albite ($Na_2O \cdot Al_2O_3 \cdot 6SiO_2$). It is the albite (and other feldspars) in granite that cause it to be an outlying point in much of the previous analysis. For instance, the granite (GR) and Vega (VG) aggregates tested had thermal coefficients of 10.3 and 11.7 microstrains/°C (5.7 and 6.5 microstrains/°F), respectively, yet GR has an SiO_2 residue of 71.3 percent versus 66.9 percent for VG. Since quartz is so thermally expansive, this is counterintuitive. Because the breakdown of albite yields additional SiO_2, granite appears to have had the second highest mineral quartz

FIGURE 3 Parametric curves for blend design (example).

TABLE 1 Mineral Composition of Phase II Aggregates

Source	Aggregate Type	Most Abundant	Second	Third
McCelligan # 1	DL	Dolomite	Calcite	Quartz
Western-Tascosa	WT	Quartz	Calcite	
Tin-Top # 1	BTT	Calcite	Quartz	
Bridgeport	BTT	Calcite	Dolomite	Quartz
Feld (TCS)	LS	Calcite	Dolomite	Quartz
Fordyce	SRG	Quartz	Calcite	
Vega	VG	Quartz	Calcite	
Ferris # 1	FR	Calcite	Quartz	
Scotland Granite	GR	Quartz	Albite	

content of the tested aggregates; however, this is not the case. Much of the SiO_2 residue came from albite, not quartz. Albite and quartz have very different physical properties (such as thermal coefficient of expansion). The technique presented here will eliminate this type of problem.

Assumptions

Mined aggregate is a complex blend of many minerals; it would be impossible from the rudimentary information given in Table 1 to determine the exact mineral composition of the aggregates. Fortunately, a methodology to backcalculate the principal minerals should be all that is needed to develop more robust models.

Accordingly, the following imprecise but essentially correct assumptions were made:

1. All SiO_2 residue in the sample came from quartz or feldspar (granite is composed of quartz and feldspar). Only the two most commonly occurring types of feldspars, albite (the sodic plagioclase feldspar) and orthoclase and microcline potassium feldspars, chemically ($K_2O \cdot Al_2O_3 \cdot 6SiO_2$), were considered in this analysis. Orthoclase and microcline have the same chemical composition but differ in crystalline structure.

2. All CaO residue in the sample came from calcite or dolomite.

Reactions

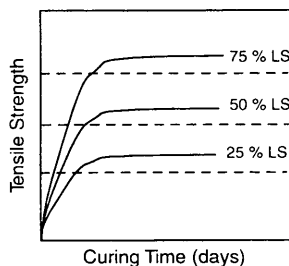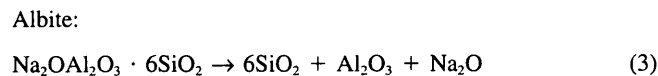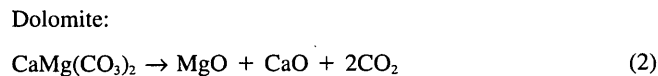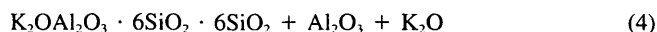The two foregoing assumptions imply the following decompositions:

Calcite:

$$CaCO_3 \rightarrow CaO + CO_2 \tag{1}$$

Dolomite:

$$CaMg(CO_3)_2 \rightarrow MgO + CaO + 2CO_2 \tag{2}$$

Albite:

$$Na_2OAl_2O_3 \cdot 6SiO_2 \rightarrow 6SiO_2 + Al_2O_3 + Na_2O \tag{3}$$

Potassium feldspars:

$$K_2OAl_2O_3 \cdot 6SiO_2 \cdot 6SiO_2 + Al_2O_3 + K_2O \quad (4)$$

Computational Method: Carbonates

Using the molecular weights for the compounds (Table 2) and the balanced equations above, it is a simple matter to determine the weight ratios relating the oxides to the original mineral content. For instance, from Equation 2 it can be seen that dolomite breaks down to MgO in a one-to-one ratio. That is, each mole of dolomite produces one mole of magnesium oxide.

Since the molecular weight of dolomite is 184.407 and the molecular weight of MgO is 40.305, 184.407/40.305 = 4.575 g of dolomite must have existed for each gram of MgO in the original sample.

$$\text{Dolomite (g)} = \text{MgO (g)} \cdot 4.5752 \quad (5)$$

In order to estimate the original calcite in the sample, it is first necessary to subtract the amount of CaO produced from dolomite (CaO_{dol}). The decomposition of dolomite yields CaO in a 1:1 molar ratio, or 56.08 g CaO/184.407 g dolomite = 0.3041.

$$CaO_{dol} \text{ (g)} = \text{dolomite (g)} \cdot 0.3041 \quad (6)$$

Then, CaO from the decomposition of calcite (CaO_{cal}) equals the total CaO (CaO_{tot}) less the amount released from dolomite:

$$CaO_{cal} \text{ (g)} = CaO_{tot} \text{ (g)} - CaO_{dol} \text{ (g)} \quad (7)$$

Now that CaO_{cal} is known, the original percent calcite (limestone) can be calculated. In a 1:1 ratio, 1 mole (100.091 g) of calcite produces 1 mole (56.08) of CaO, giving a molecular weight ratio of 100.091/56.08 = 1.785.

$$\text{Calcite (g)} = CaO_{cal} \text{ (g)} \cdot 1.785 \quad (8)$$

Computational Method: Silicates

A similar process can be employed to determine the original silicate content. First, assuming most or all Na_2O was produced by

the breakdown of albite (see Table 1), the following formula is given:

$$\text{Albite (g)} = Na_2O \text{ (g)} \cdot 8.46 \quad (9)$$

Assuming most or all K_2O was produced by the breakdown of potassium feldspars (PF) such as orthoclase and microcline,

$$\text{PF (g)} = K_2O \text{ (g)} \cdot 5.8 \quad (10)$$

Calculating SiO_2 from albite [$SiO_{2(alb)}$]:

$$SiO_{2(alb)} \text{ (g)} = \text{albite (g)} \cdot 0.6874 \quad (11)$$

Calculating SiO_2 from potassium feldspars [$SiO_{2(PF)}$]:

$$SiO_{2(PF)} \text{ (g)} = \text{PF (g)} \cdot 0.6595 \quad (12)$$

Then the remaining SiO_2 must have been quartz before testing:

$$\text{Quartz (g)} = SiO_{2(tot)} \text{ (g)} - SiO_{2(alb)} \text{ (g)} - SiO_{2(PF)} \text{ (g)} \quad (13)$$

Results

Percentages after decomposition for the eight aggregates are given in Table 3. A computer program written in the SAS language was developed to calculate mineral content according to Equations 5–13. The results of running this program on the oxide residue data are given in Table 3. As a check of the methodology, the remaining unexplained mineral content is given in the last column.

DISCUSSION OF RESULTS

In general, the procedure performs very well in describing the mineral content of the original sample. No conflict was found with the original crystallography analysis (Table 1). Most of the oxide residue was accounted for, with a maximum of 8.96 percent unexplained for aggregate (FR). This is probably due to the large

TABLE 3 Calculated Percent Mineral Composition

Aggregate	Calcite	Dolomite	Quartz	Albite	PF	Unexplained
BTT	73.98	3.245	15.51	1.269	1.77	4.23
DL	29.87	59.42	5.01	0.76	1.54	4.3
FR	73.87	1.97	12.22	1.44	1.54	8.96
GR	1.11	2.88	31.05	37.23	22.63	5.1
LS	66.53	27.29	0.94	1.18	1.24	2.82
SRG	3.70	0.50	91.53	1.52	1.89	0.86
VG	19.68	1.78	56.93	8.04	6.86	6.71
WT	19.42	1.60	59.35	7.19	6.50	5.94

TABLE 2 Molecular Weights for Selected Compounds

Compound	Molecular Weight (g)
Calcite	100.091
Dolomite	184.407
Quartz	60.0855
Albite	524.48
PF	546.674
CaO	56.08
MgO	40.305
SiO_2	60.086

amount of ferric minerals found in this aggregate, which were not addressed in the analysis.

THERMAL COEFFICIENT MODEL

Using the estimated mineral content from the stoichiometric procedure (Table 4), regression was used to model thermal coefficient of expansion (α_c) as a function of mineral content in the sample:

$$\alpha_c = e^{1.098} \cdot (quartz)^{0.486} \cdot (calcite)^{-0.106} \cdot (dolomite)^{0.415}$$
$$\cdot (PF)^{-2.37} \cdot (albite)^{1.635} \qquad (14)$$

where

      quartz = percent quartz by weight,
      calcite = percent calcite by weight,
   dolomite = percent dolomite by weight,
        PF = percent potassium feldspars by weight,
     albite = percent albite by weight, and
       FS = albite + PF, all feldspars by weight.

α_c is in microstrains per degree Fahrenheit and can be converted to degrees Celcius by multiplying by 1.8.

Figure 4 shows the fit for the thermal coefficient model. This model has been tested on several additional aggregates and provides reasonable predictions in most cases. Additional models for tensile strength, compressive strength, and elastic modulus were also fit by a similar method:

$$f_c \text{ (psi)} = e^{8.943} \cdot (calcite)^{-0.086} \cdot (quartz)^{-0.072}$$
$$\cdot (dolomite)^{-0.021} \cdot (FS)^{-0.033} \qquad (15)$$

$$f_t \text{ (psi)} = 1298 - 8.87 \cdot (calcite)^{-8.089} \cdot (quartz)^{-7.45}$$
$$\cdot (dolomite)^{-49.8} \cdot (PF) + 16.6 \cdot (albite) \qquad (16)$$

$$E \text{ (psi, millions)} = e^{1.115} \cdot (calcite)^{-0.0087} \cdot (quartz)^{0.121}$$
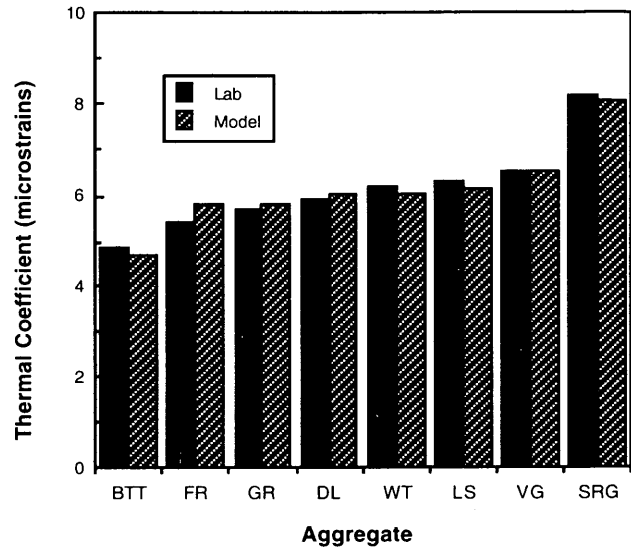$$\cdot (dolomite)^{0.088} \cdot (FS)^{-0.101} \qquad (17)$$

FIGURE 4 Fit for thermal coefficient model (Equation 14).

The terms f_c, f_t, and E can be converted from pounds per square inch to kilopascals by multiplying by 6.9.

It must be stressed that the models were developed using only the Phase II laboratory data (eight Texas aggregates) and thus are very restricted in terms of inference space. It is expected that additional laboratory and field data being collected at this time (Phase III testing) will allow improvement of the model. In particular, as suggested earlier, separate models will be developed for siliceous and calcareous aggregates, which should greatly strengthen their predictive ability.

CONCLUSIONS AND RECOMMENDATIONS

The models given here for thermal coefficient, compressive strength, tensile strength, and elastic modulus are preliminary and

TABLE 4 Phase II Chemical Analysis Results

Source	Aggregate Type	Type	SiO_2	CaO	MgO	CO_2	MnO	Fe_2O_3	Al_8O_3	Na_2O	K_2O	TiO_2	Other
McKelligan	Dolomite	(DL)	6.53[a]	34.9	13.0	42.9	.02	0.21	0.38	0.09	0.26	0.02	1.69
Western-T	S/L	(WT)	68.5	11.4	0.35	8.98	.05	2.64	3.97	0.85	1.1	0.17	1.99
Bridpt+TinTop	L+S/L	(BTT[b])	17.53	42.55	0.71	35.65	0.04	0.57	0.56	0.15	0.30	0.04	1.91
Feld (TCS)	Limestone	(LS)	2.56	45.7	5.97	43.3	.01	0.06	0.21	0.14	0.21	0.02	1.82
Fordyce	SRG	(SRG)	93.8	2.23	0.11	1.77	.01	0.76	0.63	0.18	0.32	0.1	0.09
Vega	SRG	(VG)	66.9	11.6	0.39	9.07	.07	2.33	4.22	0.95	1.16	0.19	3.12
Ferris	L/S	(FR)	14.2	42.1	0.43	34.4	.10	3.70	0.87	0.17	0.26	0.06	3.71
Scotland	Granite	(GR)	71.3	1.5	0.63	0.59	.03	1.52	14.3	4.4	3.83	0.29	1.61

[a]All values are percent by weight.

[b]These aggregates combined in a 50/50 blend when tested in the laboratory for concrete properties.

serve only to demonstrate the two-stage procedure in which mineral content is first backcalculated and then used to estimate concrete material properties. However, the stoichiometric methodology developed (CHEM2) is a significant improvement over direct regression techniques using oxide residue analysis (e.g., CHEM1). As more data become available, the regression models predicting concrete performance from aggregate mineral content will continue to be improved until they are able to predict reliably over a wide range of aggregate types.

CHEM2 offers the pavement designer the opportunity to estimate the performance of new, untried aggregates before undergoing the expense of full concrete testing. At the time of this writing, the oxide residue test needed to run CHEM2 cost less than $100. Of course, CHEM2 is not intended to replace conventional testing procedures.

ACKNOWLEDGMENTS

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