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PORTLAND CEMENT ASSOCIATION **Research and Development Division MANUFACTURING PROCESS DEPARTMENT**

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Slide Rule For Calculating Potential Compound Composition of

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Portland Cement



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PORTLAND CEMENT ASSOCIATION Research and Development Laboratories

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Portland Cement Potential Compound Slide Rule

SLIDE RULE FOR CALCULATING POTENTIAL COMPOUND COMPOSITION OF PORTLAND CEMENT

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Introductory Remarks

The slide rule described herein was designed for converting percentages of the major oxides in portland cement and cement clinker into percentages of compounds present in the clinker at crystalline equilibrium. The rule was designed by L. A. Dahl (Rock Products, November 9, 1929, page 50). The compounds involved were reported, with arithmetical and graphic methods for performing the same conversion, by R. H. Bogue (Industrial and Engineering Chemistry, Analytical Edition, Vol. 1 (1929), page 192, and Rock Products, November 9, 1929, page 47). Reference should be made to these papers for details concerning the design of the rule and the selection of compounds into which the conversion is made.

The slide rule is designed for a portion of the system 3CaO.SiO₂-2CaO.SiO₂-3CaO.Al₂O₃-4CaO.Al₂O₃.Fe₂O₃ which includes most portland cement compositions (considered with reference to the four major oxides in cement clinker). In this range, percentages of the compounds are obtained directly. The rule may be applied to "over-limed" compositions, involving CaO instead of 2CaO.SiO₂, by simple additional computations which will be described. A method of using the slide rule for compositions in an adjacent system involving 2CaO.Fe₂O₃ instead of 3CaO.Al₂O₃ has been devised by R. H. Bogue. A scale for 2CaO.Fe₂O₃ has been introduced in the slide rule for use with this method.

Compounds Formed in Cement Clinker. In the investigation reported by R. H. Bogue, referred to above, it was found that in systems involving only the principal oxide constituents of portland cement clinker, CaO, SiO_2 , Al_2O_3 , Fe_2O_3 and MgO, the compounds present at crystalline equilibrium are the following:

- (1) Tricalcium silicate, 3CaO.SiO2.
- (2) Dicalcium silicate, 2CaO.SiO2.

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- (3) Tetracalcium aluminoferrite, 4CaO.Al203.Fe203.
- (1,) Magnesia, essentially uncombined, MgO.
- (5) Tricalcium aluminate, 3CaO.Al₂O₃, or dicalcium ferrite, 2CaO.Fe₂O₃. Tricalcium aluminate is present only when the number of equivalents of Al₂O₃ exceeds that of Fe₂O₃, dicalcium forrite then being absent. In some unusual cases, the number of equivalents of Fe₂O₃ exceeds that of Al₂O₃. In that case, dicalcium forrite is present (in solid solution with $UCaO.Al_2O_3$), while tricalcium aluminate is absent.

Naturally the calculated compound composition is in error to the extent that the percentages of the compounds are influenced by the minor constituents and by failure to attain crystalline equilibrium. Questions have also arisen concerning the state of Fe_20 and Al_2O_3 .* However, notwithstanding the present uncertainty concerning these matters, the potential compound composition calculated upon the basis of the compounds listed above has been found to be of great value in control of composition in the manufacturing process and in comparisons of the behavior of portland coments.

Insoluble Residue. The "insoluble residue" obtained in a cement analysis may be composed of silica in the form of quartz together with titania and other components which are present in traces. This silica is not in combination, and consequently may be deducted from the total silica before proceeding with the computation. However, with the small amount of insoluble residue usually found, from 0.1 to 0.2%, it is generally not advisable to determine the amount of silica which it contains. Unless the amount of residue is large anough to warrant determination of its SiO₂ content, it should be ignored. The effect of ignoring small quantities of SiO₂ may be estimated from the fact that a plus error of 0.1% of SiO₂ will result in a decrease of 0.76% in computed 3CaO.SiO₂, and an increase of 0.06% in 2CaO.SiO₂.

Free CaO in Clinker. The free CaO content of clinker may be determined by the method described by Lerch and Bogue (Industrial and Engineering Chemistry, Analytical Edition, Vol. 2 (1930), page 296. The free CaO found by this method is CaO which has failed to combine with any other of the components of the clinker, and is consequently designated as "free". If the intention in calculating compounds is to use the converted composition in studying cement properties, the free CaO should be determined and deducted from total CaO before proceeding with the computations. On the other hand, if the purpose is to judge control of composition in the manufacture of cement, no deduction of free CaO or silica in insoluble residue is necessary. Deducting 1.00% free CaO from the total CaO results in a decrease of 4.07% in computed 3CaO.SiO₂ and an increase of 3.07% in 2CaO.SiO₂.

Free CaO in Cement. The method of Lerch and Bogue for determining free CaO is frequently applied to portland comment. The value obtained is usually not the true free CaO content, however, since it includes $Ca(OH)_2$, a product of hydration which is not free CaO, and the value is reduced by carbonation of $Ca(OH)_2$ and free CaO when comment is exposed to the air. The value obtained in the test may therefore be greater or less than the free CaO content of the clinker from which the comment is made. The extent of the error introduced by ignoring free CaO, or by deducting the per cent obtained by applying the Lerch and Bogue method to cement, may be judged by the factors given above.

*M. A. Swayze. American Journal of Science, Vol. 244, No. 1 and 2. (Jan. and Feb., 1946).

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<u>Calcium Sulfate</u>. The SO₃ in a cement is derived principally from gypsum added prior to grinding. Scales are provided on the rule for taking the SO₃ content into account when computing percentages of clinker compounds in a cement. There is no method available for distinguishing between the SO₃ originally present in the clinker and that added before grinding. It is suggested that SO₃ be taken into account in calculations involving cement, and ignored in calculations involving clinker.

Application to Cement Raw Mixtures. The slide rule may be applied to cement raw mixtures after conversion of the oxide composition to an ignited basis. In this application the compound composition obtained represents the percentages of the compounds which would be present if the principal oxides were converted completely to the compounds named, with no loss or gain of the individual oxides. Since complete conversion is assumed, there is no need for considering free CaO or any other product of incomplete combination. The percentages of some of the oxides will frequently be outside of the range of the scales on the rule. Methods of using the slide rule in such instances are available to those who have occasion to deal with conditions of this nature.

Operation of Slide Rule

The following abbreviations are used:

$$C_{3}A = 3CaO_{*}Al_{2}O_{3}$$

 $C_{2}F = 2CaO_{*}Fe_{2}O_{3}$
 $C_{4}AF = hCaO_{*}Al_{2}O_{3} \cdot Fe_{2}O_{3}$
 $C_{3}S = 3CaO_{*}SiO_{2}$
 $C_{2}S = 2CaO_{*}SiO_{2}$

In describing the operation of the slide rule, the guide lines at the ends of the scales are regarded as the ends of the rule and of the slide. When it is stated that the runner is to be set over the end of the slide, it is understood that the hair line on the runner is to be placed over the guide line at one end of the slide, always choosing the end which does not project beyond the end of the rule.

The scales for calculating C_3S and C_2S are on the face of the rule. Those for the other compounds are on the back of the rule. Unlike previous models of the slide rule, it is unnecessary to reverse the slide at any time.

Cements manufactured in this country are generally of the type in which the Al_2O_3/Fe_2O_3 ratio is greater than O_2O_4 . These will be referred to as C_3A cements, since C_3A is present and C_2F absent. Cements with an Al_2O_3/Fe_2O_3 ratio less than O_2O_4 present, C_3A absent) are seldom encountered. The slide rule may be applied to both classes of composition. There are some differences in the operation of the slide rule for the two types of composition, and where these differences occur, the successive steps will be shown side by side, with those for the C_A compositions at the left. For the usual compositions, in which C_A is present, the procedure described at the right may be ignored.

Tricalcium Aluminate (C_2A) or Dicalcium Ferrite (C_2F) and Tetracalcium Alumino-Ferrite (C_2AF) . Use back of rule.

Set runner over per cent Al₂O₃.

Draw per cent Fe_2O_3 under runner. For cements of the usual type (C₃A present, C₂F absent) the slide will now project to the right. If it projects to the left, C₂F is present, C₃A absent. The procedure in the two cases is given separately below.

Slide projecting to right (CaA present)	Slide projecting to left (C2F present
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Read per cent C₄AF under runner. Set runner over end of slide.

Read per cent C_aA under runner.

Set runner over end of slide. Read per cent C₂F under runner.

Sot slide flush with rule, by means of the guide lines.

Draw runner over per cent Al₂O₃. Read per cent C₄AF under runner.

face of the rule. $\frac{\text{Tricalcium Silicate } (C_{3}S) \text{ and Dicalcium Silicate } (C_{3}S)}{\text{rule.}}$ Use the

Set runner over per cent CaO (or per cent CaO remaining after deducting free CaO).

Draw per cent SiO_2 (scale for C_3S) under runner. Set runner over end of slide.

C_A Compositions

Draw per cont Al₂O₅ under runner. Set runner over end of slide. Draw per cent Fe₂O₃ under runner. Set runner over end of slide.

C₂F Compositions

Draw 2/3 of the per cent Al₂O₃ under runner. Set runner over end of slide. Draw twice the per cent Fe₂O₃ under runner. Set runner over end of slide.

Draw per cent SO_2 under runner. Set runner over end of slide. (This step is omitted if SO_3 is to be ignored, as in the case of raw mixtures or clinker.)

Read per cent C_3S under runner, leaving the runner in place for the calculation of C_2S . If the runner is near the left hand end of the rule, the per cent of C_3S may be the value under the runner or may be 70.0 greater than that value. Experience will enable the operator to recognize at once whether 70.0 should be added. If in doubt, the value under the runner may be recorded, subject to correction when the computation is checked. (See Example 4.) Draw per cent SiO₂ (scale for C₂S) under runner. Set runner over end of slide. Read per cent C₂S under runner on the C₂S (B scale) except when the C₂S is less than 23.0 per cent or negative (over-limed cement), in which case the potential C₂S is read on the C₂S (A scale). If in doubt, both values may be recorded, subject to choice when the computation is checked. (See Example 4.)

Calcium Sulfate (CaSO₄). Use the back of the rule.

SO3.

The per cent of $CaSO_4$ is read directly below the per cent of

Magnesia (MgO). At crystalline equilibrium the magnesia in portland cement clinker is essentially uncombined. Hence, the analytical value for MgO is used directly in expressing compound composition.

<u>Checking the Computation</u>. The sum of the percentages of the compounds should be equal to the sum of the percentages of the oxides involved in the computation. This provides a convenient means of detecting errors. If the total is to be used in checking, it is necessary to manipulate the rule carefully, estimating percentages of the compounds to 0.1 per cent. The importance of this procedure may be seen by considering the effect of a plus error of 1.00 per cent in the estimation of C_sS . This introduces a minus error of 0.75 per cent in the C_2S , so that the total is increased only 0.25 per cent.

Two values for per cent C_3S are obtainable: the value read on the scale or a value 70.0 greater. Similarly, two values for C_2S are obtainable, the value on the B scale or a value 52.8 per cent less, on the A scale. Upon checking the total, the values of C_3S and C_2S which lead to a total which checks the sum of the oxides are the correct values.

Over-limed Compositions. If the per cent of CaO is above the theoretical lime limit, the calculated per cent of C_2S will be negative when composition is calculated without deducting free CaO from total CaO. Negative percentages of C_2S appear on the right-hand portion of the A scale.

The negative percentage of C_2S and the per cent of C_3S obtained with it are fictitious, but they should be used without correction in raw mix calculations. A negative C_2S in a clinker, however, indicates that at crystalline equilibrium CaO (excess lime) and C_3S are present, and C_2S absent. The per cent of excess CaO and the correct per cent of C_3S are obtained by the following procedure.

The per cent of excess CaO is one-third of the negative C_2S_3 , or more accurately, 0.3256 times the C_2S_3 .

The per cent of C_{gS} is equal to the result obtained by subtracting the per cent of CaO from the algebraic sum of the $C_{3}S$ and $C_{2}S$ obtained with the slide rule. For example, if the percentages of C_3S and C_2S obtained with the slide rule are ∂I_2 and -I2.3 per cent, respectively, the per cent of excess CaO is $I2.3 \times 0.3256$, or 4.0 per cent. The algebraic sum of ∂I_2 and -I2.3 is $\partial I_2 - I2.3$, or $\partial 8.9$. The correct percentage of C_3S is therefore $\partial 8.9 - 4.0$, or $\partial 4.9$ per cent.

Illustrations

The following examples are given to illustrate the method of computation, and also the method of checking the computation:

Oxides			Compounds	
	Analysis	As Used in Rule	compounds	
SiO ₂ Al ₂ O ₃ Fe ₂ O ₃ CaO MgO SO ₃ Free Ca	20.60 6.88 4.86 63.81 (3.00) (0.32) 20 (0.63)	20.60 6.88 4.86 63.18	$\begin{array}{cccc} C_{3}S & 47.4 \\ C_{2}S & 23.3 \\ C_{3}A & 10.0 \\ C_{4}AF & 14.8 \\ (3.0) \\ (0.6) \end{array}$	
Tota	1	95.52	95.5	

Example 1, A Clinker

The free CaO is deducted from the total CaO, which leaves 63.18 per cent CaO to be used in computing C_3S and C_2S . Values in parentheses are not included in the total, which includes only the values involved in the check.

Example 2. A Clinker of Low Al₂O/Fe₂O₃ Ratio (C₂F present)

Oxides					
	Analysis	As Used In Rule			unds
		For C2F & C4AF	For C3S & C2S		
Si0 ₂ Al ₂ 0 ₃ Fc ₂ 0 ₃ Ca0 Mg0 Free Ca0	22.48 3.75 7.08 65.31 (1.04) (.23)	3•75 7•08	22.48 2.50 14.16 65.08	C₃S C₂S C₂F C₄AF	57.0 21.5 2.1 17.9 (1.0) (0.2)
Total	98.39				98.5

In calculating C_3S , two thirds the per cent of Al_2O_3 and twice the per cent of Fe_2O_3 , that is, 2.50 and 14.16 per cent, respectively, are used. The total of the four compounds is checked against the sum of the first four oxides, less the free CaO.

Oxides		Compounds			
	Analysis	As Used in Rule		Cement	Approx. Clinker Basis
SiO ₂ Al ₂ O ₃ Fe ₂ O ₃ CaO MgO SO ₃ Ign. Loss	20.83 5.42 2.94 62.85 4.98 1.65 .84	20.83 5.42 2.94 62.85 1.65	C ₃ S C ₂ S C ₃ A C ₄ AF CaSO ₄ MgO	52.2 20.4 9.4 8.9 2.8 (5.0) (0.8)	54.4 21.3 9.8 9.3 - 5.2
Tota	1.	93.69		93.7	100.0

Example 3. A Coment

The sum of the non-volatile constituents derived from the clinker is $93.7 + MgO - CaSO_{4,}$ or 95.9. To place the cement composition on an approximate clinker basis, the percentages of the first four compounds and the MgO are each multiplied by 100/95.9, or 1.043, obtaining the figures in the last column.

Example L	1. I	In Over-	Limed	Composition
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	Oxides	Compounds		
	Per	Obtained	ned Corrected	
	cent	on Rule	As Raw Mix	As Clinker
Si02	18.83	C3S 11.8 and 81.8	81.8	71.6
Al ₂ Õ ₃	6.30	C2S 45.1 and -7.7	-7.7	
Fe ₂ 0 ₃	կ դեկ	C ₉ A 9,2	9.2	9.2
CaO	67.20	C4AF 13.5	13.5	13.5
MgO	2.74	MgO 2.7	2.7	2.7
· · ·		Excess CaO		2.5
Total	99.51		99.5	29.5

As obtained on the rule, two values are found for C_3S , 11.8 and 11.8 + 70.0, or 81.8. Similarly, two values for C_2S , 45.1 and -7.7 are found, from the B and A scales, respectively. The values 81.8 for C_3S and -7.7 for C_2S lead to the correct total, and are therefore the correct values.

The calculation proceeds no further if the material is a raw mix. If it is a clinker, the excess CaO is found as $7.7 \ge 0.3256$, or 2.5 per cent. The correct per cent of C_3S is 61.8 = 7.7 = 2.5, cr 71.6, which leaves the total unchanged.