The Calculation of Raw Mixtures in the Manufacture of Portland Cement

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In the present paper the author has tried to treat the calculation of artificial raw mixtures in the production of portland cement in a new way, and to illustrate the problem with two practical examples.

It must be pointed out that this calculation is exact only if the raw material is of uniform composition, and the technological process is carried on in a rotary kiln using gaseous or liquid fuel, i. e. fuel with a minimal content of ashes. In the case coal dust is used as fuel, the hydraulic ratio will decrease, depending on the quantity and quality of ashes present, in proportion with the increase of the silicate and other ratios.

In this case an exact treatment is particularly difficult as the decrease of hydraulic ratio mentioned above is not only a function of the composition of the ashes and the coal, but also of the heating power of the coal used, i. e. the necessary quantity of coal for the burning of clinker. But this again depends on the composition of the coal and on the burning process.

The author, however, considers this calculation useful also in processes where the heating is done by means of coal dust, because the amount of change of each particular ratio during the process of burning in a particular industrial installation and with the use of a particular coal is commonly known from experience. Besides, we can easily and quickly control the influence of ashes on the composition of the resulting clinker.

In connection with the calculation a description is given of the correction of the raw slurry in silos, in case the cement is produced by the wet process, as this is in a close relation with the first problem.

Advantages of this method as compared with those described in the literature are many:

1) Simplicity: The calculation may be done by an unskilled person using only the slide rule.

2) Great speed of calculation: Within two hours one can easily bring four components into harmony with regard to the hydraulic, silicate and aluminate ratios. Furthermore, one can obtain the yield and the composition of the burned clinker, and the percents of $CaCO_3$ in the raw mixture or in the dried raw slurry. This last detail is necessary for the eventual additional correction of the crude raw mixture or slurry.

3) Possibility of immediate control of the calculations: By using the slide rule, ratios will be obtained, if there was no miscalculation, which must correspond to the given ratios.

4 This method can be used also for the calculation of other mixtures, provided they depend on certain proportions.

5) It is not necessary to understand the given mathematical treatment of the problem, but only to apply the resulting equations in the manner illustrated in the examples.

At the end it should be noted, that with a general introduction of the calculated proportions into the final equations, certain expressions can be reduced. The author has desisted from this intentionally, because in this case he would have considerably prolonged and complicated the practical computing.

1) *Crude Mixture and Composition of Clinker.* Through the analyses of good portland cements it has been established that the hydraulic qualities depend on the proportion of basic and acid components of the cement.

Therefore the chemist Michaelis introduced the conception of hydraulic ratio (*H*), and he designed it as a proportion of calcium oxide to the sum of silicium dioxide, aluminium trioxide and iron trioxide. The best hydraulic qualities have those cements, whose hydraulic ratios are equal to 1,7—2,3. It is evident that the basic component here is CaO, and the acid components are SiO_2, Al_2O_3 and Fe_2O_3.

From this it can be deduced:

$$\text{Hydraulic ratio } \frac{CaO}{SiO_2 + Al_2O_3 + Fe_2O_3} = 1{,}7—2{,}3$$

The following abbreviations are used:

Hydraulic ratio	= H	
% SiO_2	= S	
% Al_2O_3	= A	or:
% Fe_2O_3	= F	
% MgO	= M	% of basic components = b
% CaO	= C	
% SO_3	= s	% of acid " = k
heating loss	= g	
% of moisture	= w	

Therefore:

$$H = \frac{C}{S + A + F} = \frac{b}{k} = 1{,}7 — 2{,}3$$

Later it has been found that ordinary cement is not resistant against sea water, i. e. against the action of $MgSO_4$ or other soluble sulphates, because Candlot's salt or »cement bacilus« $CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 30H_2O$ will be formed.

It is possible, however, to manufacture a cement where Candlot's salt can not be formed at all, if the whole amount or at least the greatest part of Al_2O_3 is firmly bound to Fe_2O_3 forming tetracaciumaluminateferrite $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, so called Brownmillerit.

So a new proportion, the aluminate ratio (*A*), a proportion of Al_2O_3 to Fe_2O_3, is introduced.

In the pure Brownmillerit this proportion is 0,64, or the aluminate ratio of Brownmillerit is 0,64. Of course the ordinary portland cement has an aluminate ratio greater then 0,64.

The aluminate ratio therefore is:

$$\text{Aluminate ratio} = \frac{Al_2O_3}{Fe_2O_3} \qquad \text{or: } A = \frac{A}{F}$$

The reciprocal value of aluminate ratio is the ferric ratio (F):

$$F = \frac{F}{A}$$

Kühl suggested one more ratio, the silicate ratio (S):

$$\text{Silicate ratio} = \frac{SiO_2}{Al_2O_3 + Fe_2O_3} \qquad \text{or: } S = \frac{S}{A + F}$$

The silicate ratio influences the temperature of sintering in such a way, that the raw material with a high silicate ratio requires a higher temperature for sintering. Thus with the use of a suitable silicate ratio the temperature of sintering can be regulated and the economy of heating in the process of clinker burning accordingly bettered. It is evident that the given ratios are important chemical characteristics of a raw material or a finished cement.

If portland cement is produced from the raw material in its natural state i. e. marl, it is clear that his ratios cannot be chosen at will. The quality of marl is the better, the more its ratios are near to the optimal for the respective kind of cement. This is why the cement industry began to use very early raw materials prepared in an artificial way, by mixing together several components, so that the mixture corresponds to the optimal conditions for the production of the respective kind of cement.

By mixing of two components, say limestone and clay, we can get a mixture with a given hydraulic ratio, while the other two ratios depend on the composition of the raw materials used. By mixing the two components, the raw material can be corrected only with regard to a certain ratio, and by mixing three components it can be corrected with regard to two ratios. Finally, by mixing four components the raw material can be corrected with regard to three ratios, and accordingly the properties of the burned clinker and cement can be regulated at will. In case we corrected the raw material with regard to all the three given ratios by mixing four components, its composition will still depend on the composition of each of the particular components used, while the rational composition of the clinker depends on the composition of the clinker, and on the manner of its burning and cooling.

In order to know in advance the composition of the clinker, it is necessary to calculate it from the proportions of each of the particular components and of their chemical composition.

We can thus in practice see at once, whether the mixture corresponds to the standard for portland cement, with regard to its chemical composition or not. The percentage of MgO and SO_3 in the burned clinker has to be taken into account, and probably also the amount of plaster to be added before the grinding of the clinker. This will eventualy prolong the time necessary for the setting of the cement, but at the same time the percentage of SO_3 must not exceed the maximum given by the standard for the portland cement.

I shall give now the general deduction of the equations, by means of which it is possible to calculate the proportions of the two and four raw components, and of the percentual composition of the final product. Two practical examples of mixing two and four raw components respectively are added.

a) *Mixing of two raw components to get a given hydraulic ratio.* The abbreviations used are:

H = The given hydraulic ratio of the mixture and clinker
G_1 = The quantity of the limestone in kilograms
G_2 = The quantity of the clay in kilograms
b_1 = % of CaO in the limestone = C_1
b_2 = % of CaO in the clay = C_2
k_2 = % SiO_2 + % Al_2O_3 + % Fe_2O_3 in the limestone = $S_1 + A_1 + F_1$
k_2 = % SiO_2 + % Al_2O_3 + % Fe_2O_3 in the clay = $S_2 + A_2 + F_2$

It follows:

$$H = \frac{G_1b_1 + G_2b_2}{G_1k_1 + G_2k_2}; \quad (G_1k_1 + G_2k_2)\,H = G_1b_1 + G_2b_2$$

$$HG_1k_1 - G_1b_1 = G_2b_2 - HG_2k_2; \qquad G_1\,(Hk_1 - b_1) = G_2\,(b_2 - Hk_2)$$

$$\frac{G_1}{G_2} = \frac{b_2 - Hk_2}{Hk_1 - b_1} = \frac{Hk_2 - b_2}{b_1 - Hk_1} = n \quad \ldots \quad (1)$$

$$G_1 = G_2 \,.\, n \quad \ldots \quad (2)$$

The proportion of mixing in percents:

$G_1 = G_2 \,.\, n$

$G_1 + G_2 = 100$

The solution of this two equations are:

$$G_1 = 100\left(1 - \frac{1}{n+1}\right)\ \% \quad \ldots \quad (3)$$

$$G_2 = \frac{100}{n+1}\ \% \quad \ldots \quad (4)$$

The calculation of the composition of the clinker:

The quantity of a given component in % in the clinker is :

$SiO_2 = 1/100\,(G_1S_1 + G_2S_2)$
$Al_2O_3 = 1/100\,(G_1A_1 + G_2A_2)$
$Fe_2O_3 = 1/100\,(G_1F_1 + G_2F_2)$
$MgO = 1/100\,(G_1M_1 + G_2M_2)$
$CaO = 1/100\,(G_1C_1 + G_2C_2)$
$SO_3 = 1/100\,(G_1s_1 + G_2s_2)$

The quantity of clinker in % is:

$$G = \frac{1}{100} [G_1 (S_1+A_1+F_1+M_1+C_1+s_1) + G_2(S_2+A_2+F_2+M_2+C_2+s_2)]$$

$$G = \frac{1}{100} [G_1(100 - g_1 - w_1) + G_2 (100 - g_2 - w_2)]$$

Therefore

$$\% \, SiO_2 = \frac{100 \, G_2 \, (nS_1 + S_2)}{G_2[n(100-g_1-w_1) + 100-g_2-w_2]} =$$

$$= \frac{100 \, (nS_1 + S_2)}{n \, (100-g_1-w_1)+100-g_2-w_2} =$$

$$= \frac{100 \, (nS_1 + S_2)}{100n-ng_1-nw_1 + 100-g_2-w_2} = \frac{100 \, (nS_1 + S_2)}{100 \, (n+1) - n(g_1+w_1)-g_2-w_2}$$

The composition of the clinker is:

$$\% \, SiO_2 = \frac{100 \, (nS_1 + S_2)}{100 \, (n + 1) - n \, (g_1 + w_1) - g_2 - w_2} \quad . \; . \; . \; . \; . \; . \; . \quad (5)$$

$$\% \, Al_2O_3 = \frac{100 \, (nA_1 + A_2)}{100 \, (n + 1) - n \, (g_1 + w_1) - g_2 - w_2} \quad . \; . \; . \; . \; . \; . \; . \quad (6)$$

$$\% \, Fe_2O_3 = \frac{100 \, (nF_1 + F_2)}{100 \, (n + 1) - n \, (g_1 + w_1) - g_2 - w_2} \quad . \; . \; . \; . \; . \; . \; . \quad (7)$$

$$\% \, MgO = \frac{100 \, (nM_1 + M_2)}{100 \, (n + 1) - n \, (g_1 + w_1) - g_2 - w_2} \quad . \; . \; . \; . \; . \; . \; . \quad (8)$$

$$\% \, CaO = \frac{100 \, (nC_1 + C_2)}{100 \, (n + 1) - n \, (g_1 + w_1) - g_2 - w_2} \quad . \; . \; . \; . \; . \; . \; . \quad (9)$$

$$\% \, SO_3 = \frac{100 \, (ns_1 + s_2)}{100 \, (n + 1) - n \, (g_1 + w_1) - g_2 - w_2} \quad . \; . \; . \; . \; . \; . \; . \quad (10)$$

% of $CaCO_3$ in the raw dry slurry:

$$\% \, CaCO_3 = \frac{178{,}5 \, (n \, C_1 + C_2)}{100 \, (n + 1) - nw_1 - w_2} \quad . \; . \; . \; . \; . \; . \; . \quad (9a)$$

The yield in clinker is:

$$G_k = 100 - \frac{1}{100} [G_1 \, (g_1 + w_1) + G_2 \, (g_2 + w_2)] \quad . \; . \; . \; . \quad (9b)$$

The mixing of two raw components to get a given silicate ratio (*S*).

According to previous mixing we have:

$$S = \frac{S}{A + F} \qquad \frac{G_1}{G_2} = \frac{S_2 - S\,(A_2 + F_2)}{S\,(A_1 + F_1) - S_1} = n' \quad . \quad . \quad . \quad . \qquad (11)$$

$$G_1 = G_2 n' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (12)$$

The mixing of two raw components to get a given aluminate ratio (A).

$$A = \frac{A}{F} \qquad \frac{G_1}{G_2} = \frac{A_2 - AF_2}{AF_1 - A_1} = n'' \quad . \quad . \quad . \quad . \quad . \quad . \qquad (13)$$

$$G_1 = G_2\, n'' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (14)$$

Example 1) An artificial raw material with the hydraulic ratio H=2,02 is to be obtained by mixing of limestone and clay. Besides, the composition of the clinker and the yield of the process should be calculated. The composition of the limestone and clay is:

	I. Limestone	II. Clay
S	2.5%	55.7%
A	1.4%	17 2%
F	1.1%	8.3%
M	0.2%	2,4%
C	53 0%	1.4%
s	0 0%	1.6%
g	40 0%	3.0%
w	1.8%	7.1%
alcal.	0,0%	3,3%

Using the equation (1) we will calculate first the rate n.

$b_1 = 53{,}0 \qquad k_1 = 5{,}0$

$b_2 = 1{,}4 \qquad k_2 = 81{,}2$

$$n = \frac{2{,}02 \,.\, 81{,}2 - 1{,}4}{53.0 - 2{,}02 \,.\, 5} = \frac{162{,}6}{42{,}9} = 3{,}79$$

Using (3) and (4) we get percents of the used raw components in the resulting mixture.

$$G_1 = 100\left(1 - \frac{1}{4{,}79}\right) = 100 \,.\, 0{,}791 = 79{,}1\%$$

$$G_2 = \frac{100}{4{,}79} = 20{,}9\%$$

For every 100 kilogram of the raw mixture, we shall use 79,1 kilogram of limestone, and 20,9 kilogram of clay.

For the comp ition of the clinker we use: (5), (6), (7), (8), (9) and (10)

$$SiO_2 = \frac{517}{310} = 21{,}0\%$$

$$CaO = \frac{20200}{310} = 65{,}2\%$$

$$Al_2O_3 = \frac{2240}{310} = 7{,}2\%$$

$$MgO = \frac{310}{310} = 1{,}0\%$$

$$Fe_2O_3 = \frac{1245}{310} = 4{,}1\%$$

$$SO_3 = \frac{155{,}5}{310} = 0{,}5\%$$

$$\text{alk.} = \frac{310}{310} = 1{,}0\%$$

The control of the calculations: $H = \frac{65{,}2}{32{,}3} = 2{,}02$ The calculation is correct!

The percentage of $CaCO_3$ in the dried raw slurry using (9a):

$$CaCO_3 = \frac{178{,}5\ (3{,}79 \cdot 53 - 1{,}4)}{465{,}1} = \frac{178{,}5 \cdot 199{,}6}{465{,}1} = 76{,}5\%$$

Out of 100 kilogram of the raw mixture we will get G_k kilogram of clinker. Using (9b):

$$G_k = 100 - \frac{1}{100}(79{,}1 \cdot 41{,}8 + 20{,}9 \cdot 10{,}1) = 100 - 35{,}21 = 64{,}79 \text{ kilogram}$$

The yield is 64,79%!

According to the calculation of the composition of clinker for the above mixture of components, one can see that the mixture would give a good portland cement.

b) The mixing of four raw components to get a raw mixture with the given hydraulic, silicate and aluminate ratios.

I.	II.	III.	IV.
$S_1\%$	$S_2\%$	$S_3\%$	$S_4\%$
$A_1\%$	$A_2\%$	$A_3\%$	$A_4\%$
$F_1\%$	$F_2\%$	$F_3\%$	$F_4\%$
$M_1\%$	$M_2\%$	$M_3\%$	$M_4\%$
$C_1\%$	$C_2\%$	$C_3\%$	$C_4\%$
$g_1\%$	$g_2\%$	$g_3\%$	$g_4\%$
$s_1\%$	$s_2\%$	$s_2\%$	$s_4\%$
$w_1\%$	$w_2\%$	$w_3\%$	$w_4\%$

The quantities of the raw components are G_1, G_2, G_3, and G_4.

The component I. is a component with an excess of CaO, *i. e.* with a high H — for instance limestone

The component II. is a component with an excess of SiO_2, *i. e.* with a high S — for instance sand clay

The component III. is a component with an excess of Al_2O_3, *i. e.* with a high A — for instance aluminous clay

The component IV. is a component with an excess of Fe_2O_3, *i. e.* with a high F — for instance iron ore.

The components II., III., and IV. are brought by means of the component I. (limestone) to the given hydraulic ratio:

Using (1) we have:

Mixture I, II $$\frac{G_1^{I\,II}}{G_2} = \frac{C_2 - H(S_2 + A_2 + F_2)}{H(S_1 + A_1 + F_1) - C_1} = n_1 \qquad (15)$$

Mixture I, III $$\frac{G_1^{I\,III}}{G_3} = \frac{C_3 - H(S_3 + A_3 + F_3)}{H(S_1 + A_1 + F_1) - C_1} = n_2 \qquad (16)$$

Mixture I, IV $$\frac{G_1^{I\,IV}}{G_4} = \frac{C_4 - H(S_4 + A_4 + F_4)}{H(S_1 + A_1 + F_1) - C_1} = n_3 \qquad (17)$$

The composition of the three mixtures in the raw state is:

Mixture I, II.: $$S_1' = \frac{G_1^{I\,II} S_1 + G_2S_2}{G_1^{I\,II} + G_2} = \frac{n_1G_2S_1 + G_2S_2}{n_1G_2 + G_2} = \frac{n_1S_1 + S_2}{n_1 + 1}$$

The analytical composition of the three mixtures is:

	I, II		I, III		I, IV	
% SiO_2	$\frac{n_1S_1 + S_2}{n_1 + 1}$	$= S_1' = S_1''$	$\frac{n_2S_1 + S_3}{n_2 + 1}$	$= S_2'$	$\frac{n_3S_1 + S_4}{n_3 + 1}$	$= S_2''$
% Al_2O_3	$\frac{n_1A_1 + A_2}{n_1 + 1}$	$= A_1' = A_1''$	$\frac{n_2A_1 + A_3}{n_2 + 1}$	$= A_2'$	$\frac{n_3A_1 + A_4}{n_3 + 1}$	$= A_2''$
% Fe_2O_3	$\frac{n_1F_1 + F_2}{n_1 + 1}$	$= F_1' = F_1''$	$\frac{n_2F_1 + F_3}{n_2 + 1}$	$= F_2'$	$\frac{n_3F_1 + F_4}{n_3 + 1}$	$= F_2''$
% CaO	$\frac{n_1C_1 + C_2}{n_1 + 1}$	$= C_1' = C_1''$	$\frac{n_2C_1 + C_3}{n_2 + 1}$	$= C_2'$	$\frac{n_3C_1 + C_4}{n_3 + 1}$	$= C_2''$

By mixing the mixture I, II with the mixture I, III we get the mixture I, II, III, which has the given H and S:

The weight of the mixture I, II $= G_1'$

The weight of the mixture I, III = G_2'

Using (11) we have:

$$\frac{G_1'}{G_2'} = \frac{S_2' - S\,(A_2' + F_2')}{S\,(A_1' + F_1') - S_1'} = \frac{\dfrac{n_2S_1 + S_3}{n_2 + 1} - S\,\dfrac{n_2A_1 + A_3 + n_2F_1 + F_3}{n_2 + 1}}{S\,\dfrac{n_1A_1 + A_2 + n_1F_1 + F_2}{n_1 + 1} - \dfrac{n_1S_1 + S_2}{n_1 + 1}}$$

$$\frac{G_1'}{G_2'} = \frac{(n_1 + 1)\,[n_2S_1 + S_3 - S\,(n_2A_1 + n_2F_1 + A_3 + F_3)]}{(n_2 + 1)\,[S\,(n_1A_1 + n_1F_1 + A_2 + F_2) - n_1S_1 - S_2]} = n_1' \qquad (18)$$

By mixing the mixture I, II with the mixture I, IV we get the mixture I, II, IV, which has the given H and S:

The weight of the mixture I, II = G_1''
The weight of the mixture I, IV = G_2''

Using (11) we have:

$$\frac{G_1''}{G_2''} = \frac{S_2'' - S\,(A_2'' + F_2'')}{S\,(A_1'' + F_1'') - S_1''} = \frac{\dfrac{n_3S_1 + S_4}{n_3 + 1} - S\,\dfrac{n_3A_1 + A_4 + n_3F_1 + F_4}{n_3 + 1}}{S\,\dfrac{n_1A_1 + A_2 + n_1F_1 + F_2}{n_1 + 1} - \dfrac{n_1S_1 + S_2}{n_1 + 1}}$$

$$\frac{G_1''}{G_2''} = \frac{(n_1 + 1)\,[n_3S_1 + S_4 - S\,(n_3A_1 + n_3F_1 + A_4 + F_4)]}{(n_3 + 1)\,[S\,(n_1A_1 + n_1F_1 + A_2 + F_2) - n_1S_1 - S_2]} = n_2' \qquad (19)$$

The composition of the mixtures I, II, III and I, II, IV, in the raw state is:

$$S_1''' = \frac{G_1'S_1' + G_2'S_2'}{G_1' + G_2'} = \frac{G_2'n_1'S_1' + G_2'S_2'}{G_2'n_1' + G_2'} = \frac{n_1'S_1' + S_2'}{n_1' + 1}$$

$$S_2''' = \frac{G_1''S_1'' + G_2''S_2''}{G_1'' + G_2''} = \frac{n_2'S_1'' + S_2''}{n_2' + 1}$$

	I, II, III		I, II, IV	
% SiO_2	$\frac{n_1'S_1' + S_2'}{n_1' + 1}$	$= S_1'''$	$\frac{n_2'S_1'' + S_2''}{n_2' + 1}$	$= S_2'''$
% Al_2O_3	$\frac{n_1'A_1' + A_2'}{n_1' + 1}$	$= A_1'''$	$\frac{n_2'A_1'' + A_2''}{n_2' + 1}$	$= A_2'''$
% Fe_2O_3	$\frac{n_1'F_1' + F_2'}{n_1' + 1}$	$= F_1'''$	$\frac{n_2'F_1'' + F_2''}{n_2' + 1}$	$= F_2'''$
% CaO	$\frac{n_1'C_1' + C_2'}{n_1' + 1}$	$= C_1'''$	$\frac{n_2'C_1'' + C_2''}{n_2' + 1}$	$= C_2'''$

Finally, by mixing I, II, III with I, II, IV, we get the resulting mixture with the given *H*, *S* and *A*.

The weight of the mixture I, II, III = G_1'''

The weight of the mixture I, II, IV = G_2'''

Using (13) we have:

$$\frac{G_1'''}{G_2'''} = \frac{A_2''' - A\,F_2'''}{A\,F_1''' - A_1'''} = \frac{\dfrac{n_2'A_1'' + A_2'}{n_2' + 1} - A\,\dfrac{n_2'F_2'' + F_2''}{n_2' + 1}}{A\,\dfrac{n_1'F'_1 + F_2'}{n_1' + 1} - \dfrac{n_1'A'_1 + A_2'}{n_1' + 1}} =$$

$$= \frac{(n_1' + 1)\,[n_2'A_1'' + A_2'' - A\,(n_2'F_1'' + F_2'')]}{(n_2' + 1)\,[A\,(n_1'F_1' + F_2') - n_1'A_1' - A_2']} =$$

$$= \frac{(n_1' + 1)\left[n_2'\dfrac{n_1A_1 + A_2}{n_1 + 1} + \dfrac{n_3A_1 + A_4}{n_3 + 1} - A\left(n_2'\dfrac{n_1F_1 + F_2}{n_1 + 1} + \dfrac{n_3F_1 + F_4}{n_3 + 1}\right)\right]}{(n_2' + 1)\left[A\left(n_1'\dfrac{n_1F_1 + F_2}{n_1 + 1} + \dfrac{n_2F_1 + F_3}{n_2 + 1}\right) - n_1'\dfrac{n_1A_1 + A_2}{n_1 + 1} - \dfrac{n_2A_1 + A_3}{n_2 + 1}\right]} = n'' \quad (20)$$

$$G_1^{I\,II} + G_2 = G_1' + G_1'' \quad (21) \qquad G_1^{I\,III} + G_3 = G_2' \quad (22)$$

$$G_1^{I\,IV} + G_4 = G_2'' \quad (23)$$

The basis is 100 kilogram, and all weights will transform into percents.

$$G_1''' + G_2''' = 100 \quad (24) \qquad G_2'''n'' + G_2''' = 100$$

$$G_2'''\,(n'' + 1) = 100 \qquad G_2''' = \frac{100}{n'' + 1} \quad (25)$$

$$G_2''' = G_1'' + G_2'' = G_2''n_2' + G_2'' = G_2''\,(n_2' + 1) \quad (26)$$

From (25) and (26) follows:

$$G_2''\,(n_2' + 1) = \frac{100}{n'' + 1} \qquad G_2'' = \frac{100}{(n_2' + 1)\,(n'' + 1)} \quad (27)$$

From (27) and (23), and for $G_4 = \dfrac{G_1^{I\,IV}}{n_3}$ we have:

$$G_1^{I\,IV} + \frac{G_1^{I\,IV}}{n_3} = \frac{100}{(n_2' + 1)\,(n'' + 1)}$$

$$G_1^{I\,IV} = \frac{100\,n_3}{(n_3 + 1)\,(n_2' + 1)\,(n'' + 1)} \quad (28)$$

From (24):

$$G_1''' + \frac{G_1'''}{n''} = 100 \qquad G_1''' = \frac{100\,n''}{n'' + 1} \quad (29)$$

The weight of the mixture I, II, III is:

$$G_1''' = G_1' + G_2' = G_2'n_1' + G_2' = G_2' (n_1' + 1) \qquad (30)$$

From (30) and (29):

$$G_2' = \frac{100\, n''}{(n_1' + 1)\,(n'' + 1)} \qquad (31)$$

From (31) and (22), and for $G_3 = \frac{G_1^{I\,III}}{n_2}$ we have:

$$G_1^{I\,III} = \frac{100\, n'' n_2}{(n_2 + 1)\,(n_1' + 1)\,(n'' + 1)} \qquad (32)$$

In intoducing (27) and (31) in (21), and for $G_2'' = \frac{G_1''}{n_2'}$ and $G_2' = \frac{G_1'}{n_1'}$

we get:

$$G_1^{I\,II} + G_2 = \frac{100\, n'' n_1'}{(n_1' + 1)\,(n'' + 1)} + \frac{100\, n_2'}{(n_2' + 1)\,(n'' + 1)} = G_1^{I\,II} + \frac{G_1^{I\,II}}{n_1}$$

$$G_1^{I\,II} = \frac{n_1}{n_1 + 1} \left[\frac{100\, n'' n_1'}{(n_1' + 1)\,(n'' + 1)} + \frac{100\, n_2'}{(n_2' + 1)\,(n'' + 1)} \right]$$

$$G_1^{I\,II} = \frac{100\, n_1}{(n_1 + 1)\,(n'' + 1)} \left(\frac{n_1' n''}{n_1' + 1} + \frac{n_2'}{n_2' + 1} \right) \qquad (33)$$

Using (28), (32) and (33) we can calculate in percents the proportions in mixing the four given raw components, to get the mixture with the given ratios.

From (33):

$$G_2 = \frac{G_1^{I\,II}}{n_1} = \frac{100}{(n_1 + 1)\,(n'' + 1)} \left(\frac{n_1' n''}{n_1' + 1} + \frac{n_2'}{n_2' + 1} \right) \% \qquad (34)$$

From (32):

$$G_3 = \frac{G_1^{I\,III}}{n_2} = \frac{100\, n''}{(n_2 + 1)\,(n_1' + 1)\,(n'' + 1)} \% \qquad (35)$$

From (28):

$$G_4 = \frac{G_1^{I\,IV}}{n_3} = \frac{100}{(n_3 + 1)\,(n_2' + 1)\,(n'' + 1)} \% \qquad (36)$$

$$G_1 = 100 - G_2 - G_3 - G_4 \ \% \qquad (37)$$

The calculation of the composition of the clinker obtained by burning the raw mixture consisting of »i« raw components:

The percents of SiO_2: Basis is 1 kilogram

$$\% SiO_2 = \frac{\frac{\sum G_i S_i}{10\,000} 100}{1 - \frac{\sum G_i g_i + \sum G_i w_i}{10\,000}} = \frac{100 \sum G_i S_i}{10\,000 - \sum G_i g_i - \sum G_i w_i}$$

Therefrom it follows:

$$\% SiO_2 = \frac{100 \sum G_i S_i}{10\,000 - \sum G_i g_i - \sum G_i w_i} \quad \ldots\ldots \quad (38)$$

$$\% Fe_2O_3 = \frac{100 \sum G_i F_i}{10\,000 - \sum G_i g_i - \sum G_i w_i} \quad \ldots\ldots \quad (39)$$

$$\% Al_2O_3 = \frac{100 \sum G_i A_i}{10\,000 - \sum G_i g_i - \sum G_i w_i} \quad \ldots\ldots \quad (40)$$

$$\% CaO = \frac{100 \sum G_i C_i}{10\,000 - \sum G_i g_i - \sum G_i w_i} \quad \ldots\ldots \quad (41)$$

$$\% MgO = \frac{100 \sum G_i M_i}{10\,000 - \sum G_i g_i - \sum G_i w_i} \quad \ldots\ldots \quad (42)$$

$$\% SO_3 = \frac{100 \sum G_i s_i}{10\,000 - \sum G_i g_i - \sum G_i w_i} \quad \ldots\ldots \quad (43)$$

Percents of $CaCO_3$ in the raw dried slurry:

$$\% CaCO_3 = \frac{178{,}5 \sum G_i C_i}{10\,000 - \sum G_i w_i} \quad \ldots\ldots \quad (41a)$$

Rendment of the clinker burning:

$$G_k = 100 - \frac{1}{100}\left(\sum G_i g_i + \sum G_i w_i\right) \qquad \ldots\ldots \quad (41b)$$

The ratios are:

$$H = \frac{\sum G_i C_i}{\sum G_i S_i + \sum G_i A_i + \sum G_i F_i} \qquad \ldots\ldots \quad (44)$$

$$S = \frac{\sum G_i S_i}{\sum G_i A_i + \sum G_i F_i} \qquad \ldots\ldots \quad (45)$$

$$A = \frac{\sum G_i A_i}{\sum G_i F_i} \qquad \ldots\ldots \quad (46)$$

Example: 2) An artificial raw mixture is to be obtained by mixing of four raw components, with the hydraulic ratio $H = 2{,}1$, silicate ratio $S = 2{,}5$, and aluminate ratio $A = 2{,}0$. Furthermore, the composition of the clinker should be calculated, and also the yield of the process.

The composition of the raw components is:

	I	II	III	IV
S	5,0%	87,0%	30,0%	5,0%
A	2,0%	2,0%	50,0%	10,0%
F	1,0%	5,0%	0,5%	65,0%
M	1,0%	0,1%	0,2%	1,0%
C	50,0%	2,0%	1,0%	2,0%
g	40,0%	1,9%	1,3%	3,0%
s	0,1%	0,0%	1,0%	1,0%
w	0,9%	2,0%	16,0%	13,0%

The raw components are: I = Limestone, II = Sand clay, III = Aluminous clay, IV = Iron ore.

We shall first calculate all rates (i e. all »n«) from (15), (16), (17), (18), (19), and (20):

$$n_1 = \frac{2 - 2{,}1\,.\,94}{2{,}1\,.\,8 - 50} = \frac{-195{,}5}{-\ 33{,}2} = 5{,}89$$

$$n_2 = \frac{1 - 2{,}1\,.\,80{,}5}{2{,}1\,.\,8 - 50} = \frac{-168}{-33{,}2} = 5{,}06$$

$$n_3 = \frac{2 - 2{,}1\,.\,80}{2{,}1\,.\,8 - 50} = \frac{-166}{-33{,}2} = 5{,}0$$

$$n_1' = \frac{6{,}89\,[5{,}06\,.\,5 + 30 - 2{,}5\,(5{,}06\,.\,2 + 5{,}06\,.\,1 + 50 + 0{,}5)]}{6{,}06\,[2{,}5\,(5{,}89\,.\,2 + 5{,}89\,.\,1 + 7) - 5{,}89\,.\,5 - 87]} =$$

$$= \frac{6{,}89\,.\,108{,}7}{6{,}06\,.\,54{,}8} = 2{,}25$$

$$n_2' = \frac{6{,}89\,[5\,.\,5 + 5 - 2{,}5\,(5\,.\,2 + 5\,.\,1 + 10 + 65)]}{6\,[2{,}5\,(5{,}89\,.\,2 + 5{,}89\,.\,1 + 7) - 5{,}89\,.\,5 - 87]} =$$

$$= \frac{6{,}89\,.\,195}{6\,.\,54{,}8} = 4{,}08$$

$$n'' = \frac{3{,}25\left[4{,}08\,\frac{5{,}89\,.\,2 + 2}{6{,}89} + \frac{5\,.\,2 + 10}{6} - 2\left(4{,}08\,\frac{5{,}89 + 5}{6{,}89} + \frac{5 + 65}{6}\right)\right]}{5{,}08\left[2\left(2{,}25\,\frac{5{,}89 + 5}{6{,}89} + \frac{5{,}06 + 0{,}5}{6{,}06}\right) - 2{,}25\,\frac{5{,}89\,.\,2 + 2}{6{,}89} - \frac{5{,}06\,.\,2 + 50}{6{,}06}\right]} =$$

$$= \frac{3{,}25\,.\,24{,}8}{5{,}08\,.\,5{,}48} = 2{,}9$$

All calculated rates are introduced in the equations (34), (35), (36), and (37), and so the proportions in percents are obtained.

$$G_2 = \frac{100}{6{,}89\,.\,3{,}9}\left(\frac{2{,}25\,.\,2{,}9}{3{,}25} + \frac{4{,}08}{5{,}08}\right) = \frac{281{,}5}{6{,}89\,.\,3{,}9} = 10{,}45\%$$

$$G_3 = \frac{290}{6{,}06\,.\,3{,}25\,.\,3{,}9} = 3{,}78\%$$

$$G_4 = \frac{100}{6\,.\,5{,}08\,.\,3{,}9} = 0{,}84\%$$

$$G_1 = 100 - 15{,}07 = 84{,}93\%$$

Therefrom, for every 100 kilogram of the raw mixture we shall use:

I	Limestone	84,93 kilogram
II	Sand clay	10,45 kilogram
III	Aluminous clay	3,78 kilogram
IV	Iron ore	0,84 kilogram
	all together:	100,00 kilogram

Yield and the composition of burned clinker:

$$\Sigma G_i C_i = 84{,}93 \,.\, 50 + 10{,}45 \,.\, 2 + 3{,}78 \,.\, 1 + 0{,}84 \,.\, 2 = 4276$$
$$\Sigma G_i S_i = 84{,}93 \,.\, 5 + 10{,}45 \,.\, 87 + 3{,}78 \,.\, 30 + 0{,}84 \,.\, 5 = 1452$$
$$\Sigma G_i A_i = 84{,}93 \,.\, 2 + 10{,}45 \,.\, 2 + 3{,}78 \,.\, 50 + 0{,}84 \,.\, 10 = 388$$
$$\Sigma G_i F_i = 84{,}93 \,.\, 1 + 10{,}45 \,.\, 5 + 3{,}78 \,.\, 0{,}5 + 0{,}84 \,.\, 65 = 194$$
$$\Sigma G_i M_i = 84{,}93 \,.\, 1 + 10{,}45 \,.\, 0{,}1 + 3{,}78 \,.\, 0{,}2 + 0{,}84 \,.\, 1 = 88$$
$$\Sigma G_i s_i = 84{,}93 \,.\, 0{,}1 + 10{,}45 \,.\, 0 + 3{,}78 \,.\, 1 + 0{,}84 \,.\, 1 = 13$$
$$\Sigma G_i g_i = 84{,}93 \,.\, 40 + 10{,}45 \,.\, 1{,}9 + 3{,}78 \,.\, 1{,}3 + 0{,}84 \,.\, 3 = 3427$$
$$\Sigma G_i w_i = 84{,}93 \,.\, 0{,}9 + 10{,}45 \,.\, 2 + 3{,}78 \,.\, 16 + 0{,}84 \,.\, 13 = 168$$

For the control of the calculation we shall get the given rations from (44), (45) and (46):

$$H = \frac{4276}{2034} = 2{,}1 \qquad S = \frac{1452}{582}\ 2{,}5 \qquad A = \frac{388}{194} = 2{,}0$$

The calculation was correct!

From 100 kilogram of the raw mixture we will get G_k kilogram of clinker. From (41b):

$$G_k = 100 - 35{,}95 = 64{,}05 \text{ kilogram}$$

The yield is 64,05%.

The composition of the clinker from (38), (39), (40), (41), (42) and (43) is:

$$10000 - \Sigma G_i g_i - \Sigma G_i w_i = 10000 - 3595 = 6405$$

$$\% \, SiO_2 = \frac{145200}{6405} = 22{,}70$$

$$\% \, Fe_2O_3 = \frac{19400}{6405} = 3{,}03$$

$$\% \, Al_2O_3 = \frac{38800}{6405} = 6{,}05$$

The composition of the clinker is:

SiO_2	22,70%
Fe_2O_3	3,03%

$$\% \, CaO = \frac{427600}{6405} = 66,75$$

$$\% \, MgO = \frac{8800}{6405} = 1,37$$

$$\% \, SO_3 = \frac{1300}{6405} = 0,20$$

Al_2O_3	6,05%
CaO	66,75%
MgO	1,37%
SO_3	0,20%

From the calculations of the composition of the clinker one can infer that the mixture would give a good portland cement.

2) *The correction of raw slurry in silos.*

In the first part of the paper the problem was discussed of obtaining artificial raw material by mixing two or four components. The correct proportions of mixing may be obtained according to the deduced equations and also the composition of the burned clinker, produced from the calculated artificial mixture, can be calculated.

The composition of clinker obtained in such a way, however, has in general a theoretical value, because it is very dificult with the existing industrial installation effect a correct measure of the raw components, and accordingly to produce the raw material of the desired composition. Besides, raw components entering the technological process, are not of homogeneous composition, and therefore, with the variations in the composition of the components, the final product of burning, *i. e.* clinker, will also vary.

If solid fuel with its great content of ash, is used, a great deal of the ash, will enter in the composition of clinker during the process of burning and, in consequence, will have a considerable influence upon the hydraulic, silicate and aluminate ratio.

This are the reasons why a correction of the raw slurry must be effected:

In practice the slurry will be corrected only with regard to the hydraulic ratio, *i. e.* with regard to the correct percentage of $CaCO_3$ in the dried slury. The optimal quantity of $CaCO_3$ in the dried slurry can be calculated by (9a) respectively (41a), and in case of the use of solid fuel this theoretical value can be corrected still by experience.

T h e c o r r e c t i o n o f t h e s l u r r y : Besides the great silo containing the raw slurry, we have two smaller silos. One of them contains a slurry of pure limestone, *i. e.* a slurry with a great hydraulic ratio, the other contains a slurry of a clay, *i. e.* slurry with a very low hydraulic ratio. If the percentage of $CaCO_3$ of the slurry which has to be corrected is too low, a quantity of slurry with a greater hydraulic ratio must be mixed with it, while in the opposite case, the slurry with the low hydraulic ratio must be added.

The quantity of added slurry expressed in meters of silo depends on the following particulars:

1) On the composition of the slurry to be corrected

a) Participation of water in the slurry $= v_1$
b) Participation of $CaCO_3$ in the dried slurry $= c_1$
c) Spec. gravity of the slurry $= \gamma_1$ (kg/l) or (t/m³)
d) Height of the slurry in the silo $= h_1$ (m)

2) On the composition of the slurry to be used for correction

a) Participation of water in the slurry $= v_2$
b) Participation of $CaCO_3$ in the dried slurry $= c_2$
c) Spec. gravity of the slurry $= \gamma_2$ (kg/l), (t/m³)

3) On the desired composition of the corrected slurry:

a) The calculated or desired participation of $CaCO_3$ in the dried corrected slurry . . . . $= c$

The particulars mentioned above are obtained in the following manner: After a good mixing of the contents of the silo by means of compressed air, a specimen of the slurry is taken, the water evaporated and the residue dried at 105°C. Thus the amount of water in the slurry is obtained. In dividing the obtained percentage by 100, the participation of water in the slurry »v«, with the particular index is obtained.

In the residue, the calcium is determined and calculated as $CaCO_3$. The percentage of $CaCO_3$ divided by 100 gives the participation of $CaCO_3$ in the dried slurry »c« with the particular index.

The specific gravity of the slurry »γ« is determined by weighing 1 litre of the slurry, and the height of the slurry »h« is determined by measuring the upper level of the slurry in the silo.

Determination of height »h_2«, *i. e.* the height of the additional slurry used for correction: To deduce the equation, by means of which we shall correct the slurry, it is necessary to introduce certain other terms:

a) The whole weight of the uncorrected slurry $= G_1$ (t)
b) The whole weight of water in the uncorrected slurry $= V_1$ (t)
c) The whole weight of dried uncorrected slurry $= G_1'$ (t)
d) The whole weight of the slurry used for correction $= G_2$ (t)
e) The whole weight of water in the slurry used for corection $= V_2$ (t)
f) The whole weight of the dried slurry used for correction $= G_2'$ (t)
g) The cross section of the silo $= f$ (m²)

It follows:

$$G_1 = h_1 f \gamma_1 \quad V_1 = G_1 v_1 = h_1 f \gamma_1 v_1$$

$$G_2 = h_2 f \gamma_2 \quad V_2 = G_2 v_2 = h_2 f \gamma_2 v_2$$

$$G_1' = G_1 - V_1 = h_1 f \gamma_1 (1 - v_1)$$

$$G_2' = G_2 - V_2 = h_2 f \gamma_2 (1 - v_2)$$

$$\frac{G_1' c_1 + G_2' c_2}{G_1' + G_2'} = c$$

$$\frac{c_1 h_1 f \gamma_1 (1 - v_1) + c_2 h_2 f \gamma_2 (1 - v_2)}{h_1 f \gamma_1 (1 - v_1) + h_2 f \gamma_2 (1 - v_2)} = c$$

$$h_2 = \frac{h_1 \gamma_1 (1 - v_1)\ (c - c_1)}{\gamma_2 (1 - v_2)\ (c_2 - c)} \quad (m) \qquad \ldots \quad (47)$$

Example: 3) In preparing the artificial raw material according to example No. 2., the uncorrected raw slurry gives the folloving particulars:

The water in the slurry	37,0%
$CaCO_3$ in the dried slurry	77,1%
Spec. gravity of the slurry	1,63 (kg/l)
The height of the slurry in the silo	10,0 (m)

We have at disposal the following two correcting slurries:

Slurry I.	Water in the slurry	35,0%
	$CaCO_3$ in the dried slurry	98,0%
	Spec. gravity of the slurry	1,67 (kg/l).
Slurry II.	Water in the slurry	40,0%
	$CaCO_3$ in the dried slurry	4,0%
	Spec. gravity of the slurry	1,59 (kg/l)

The uncorrected raw slurry must be corrected!

It is necessary to find, in the beginning, the correct percentage of $CaCO_3$, to which we desire to correct the above mentioned slurry. This may be calculated according to (41a) as follows:

$$\% \, CaCO_3 = \frac{178{,}5\ \Sigma G_i C_i}{10000 - \Sigma G_i w_i} = \frac{178{,}5\ .\ 4276}{10000 - 168} = 77{,}8\%$$

As the corrected slurry must contain 77,8% $CaCO_3$ in the dried residue, and our uncorrected slurry contains 77,1% $CaCO_3$, the correction must be carried out with the correcting slurry No. I.

In the equation (47) we induce therefore those values:

$$v_1 = 0{,}37 \qquad v_2 = 0{,}35$$

$$c_1 = 0{,}771 \qquad c_2 = 0{,}98$$

$$\gamma_1 = 1{,}63\ (kg/l) \qquad \gamma_2 = 1{,}67\ (kg/l)$$

$$h_1 = 10{,}0\ (m) \qquad c = 0{,}778$$

$$h_2 = \frac{10 \,.\, 1{,}63 \,.\, 0{,}63 \,.\, 0{,}007}{1{,}67 \,.\, 0{,}65 \,.\, 0{,}202} = 0{,}328\ (m)$$

33 cm of the slurry I. has to be added in the silo, and its content stirred well with compressed air.

[Received, September 10, 1951]

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IZVOD

Izračunavanje smjese sirovina kod proizvodnje portland cementa

ZVONIMIR PUČAR

U ovoj radnji autor je pokušao na originalan način obraditi proračun umjetne sirovine za proizvodnju portland cementa i ilustrirati ovaj problem sa dva praktička primjera. Treba napomenuti, da ovaj proračun vrijedi egzaktno u slučaju, da raspolažemo sirovinskim komponentama jednolikog sastava, te da se pogon rotacione peći vrši pomoću plinovitog ili tekućeg goriva, t. j. goriva sa minimalnom količinom pepela. U slučaju upotrebe goriva u formi ugljene prašine, opadat će, već prema količini pepela i sastavu pepela, hidraulični modul na račun silikatnog i ostalih modula. U ovom slučaju egzaktno tretiranje naročito je otešćano time, što spomenuto opadanje hidrauličnog modula nije samo funkcija sastava pepela i ugljena, već i ogrjevne moći upotrijebljenog ugljena, t. j. potrebne količine ugljena za pečenje klinkera, a ta je opet sa svoje strane funkcija sastava ugljena i samog načina vođenja procesa pečenja.

Autor ipak smatra, da ovakav proračun može korisno poslužiti i u pogonima, gdje se loženje vrši ugljenom prašinom, jer je obično poznato iz iskustva, za koliko se mijenjaju pojedini moduli pečenjem u zadanom postrojenju i upotrebom zadanog ugljena. Osim toga se na taj način može lako i brzo vršiti kontrola utjecaja pepela na sastav klinkera.

Miješanjem dviju komponenata, na pr. vapnenca i gline, možemo dobiti smjesu sa zadanim hidrauličnim modulom, dok ostala dva modula, u tom slučaju, ovise o slučajnom sastavu upotrijebljene sirovine. Ovakvo se miješanje u praksi najviše upotrebljava. Miješanjem dviju komponenata može se sirovina korigirati samo na jedan odabrani modul, a miješanjem triju komponenata može se ona korigirati s obzirom na dva zadana modula. Konačno, miješanjem četiriju komponenata, može

se sirovina korigirati s obzirom na sva tri zadana modula, te se prema tome po volji mogu regulirati svojstva pečenog klinkera i cementa.

U koliko smo sirovinu korigirali na sva tri zadana modula, miješanjem od četiri komponente, to još uvijek kemijski sastav cementa ovisi o slučajnom sastavu pojedinih upotrijebljenih komponenata, dok racionalni sastav cementa ovisi o kemijskom sastavu cementa i o načinu pečenja i hlađenja klinkera. Da bismo unaprijed znali kemijski sastav klinkera, potrebno je isti proračunati iz omjera miješanja pojedinih komponenata, i njihovog kemijskog sastava. Na taj ćemo način u praksi odmah vidjeti, da li mješavina svojim kemijskim sastavom odgovara standardu za portland cement. Ovdje dolazi u obzir procenat MgO i SO_3 u pečenom klinkeru, te maksimalna količina sadre, koja se smije dodati prije mljevenja klinkera, da bi se produžilo vrijeme vezivanja cementa, a da pri tom procenat SO_3 u cementu ne pređe standardom dozvoljeni iznos.

U vezi sa spomenutim proračunom dan je i prikaz korekcije sirovog mulja u silosu, u slučaju proizvodnje cementa po mokrom postupku, pošto i ovaj problem stoji u tijesnoj vezi sa prvim problemom. I ovaj je slučaj ilustriran jednim praktičkim primjerom.

Prednosti navedene metode su mnogostrane:

1. Jednostavnost računanja; tako da račun može provesti i nekvalificirana osoba, pod uvjetom da se zna služiti logaritamskim računalom.

2. Brzina računanja; u roku od dva sata može se bez naročite žurbe smjesa od četiri komponente uskladiti na hidraulični, silikatni i aluminatni modul, izračunati rendement pečenja i sastav pečenog klinkera, te postotak $CaCO_3$ u sirovoj smjesi ili sušini sirovog mulja. Ovaj je posljednji podatak potreban za eventualnu naknadnu korekciju sirove smjese ili mulja.

3. Mogućnost momentane kontrole ispravnosti računanja, jer se jednim zahvatom na logaritamskom računalu dobiju moduli, koji ako nije došlo do zabune prilikom računanja, moraju odgovarati zadanim modulima.

4. Navedena metoda može se upotrijebiti i za računanje drugih smjesa, ukoliko one ovise o nekim omjerima.

5. Za računanje nije potrebno razumjeti detaljno matematički izvod metode, nego je potpuno dovoljno mehanički primijeniti odnosne rezultirajuće jednadžbe na način, kako je prikazan u priloženim primjerima.

Na kraju treba upozoriti, da bi se općenitim uvrštavanjem izračunatih omjera u konačne jednadžbe neki izrazi mogli skratiti. Autor je od toga namjerno odustao, jer bi time znatno produžio i komplicirao praktičko računanje.

Primljeno 10. rujna 1951.