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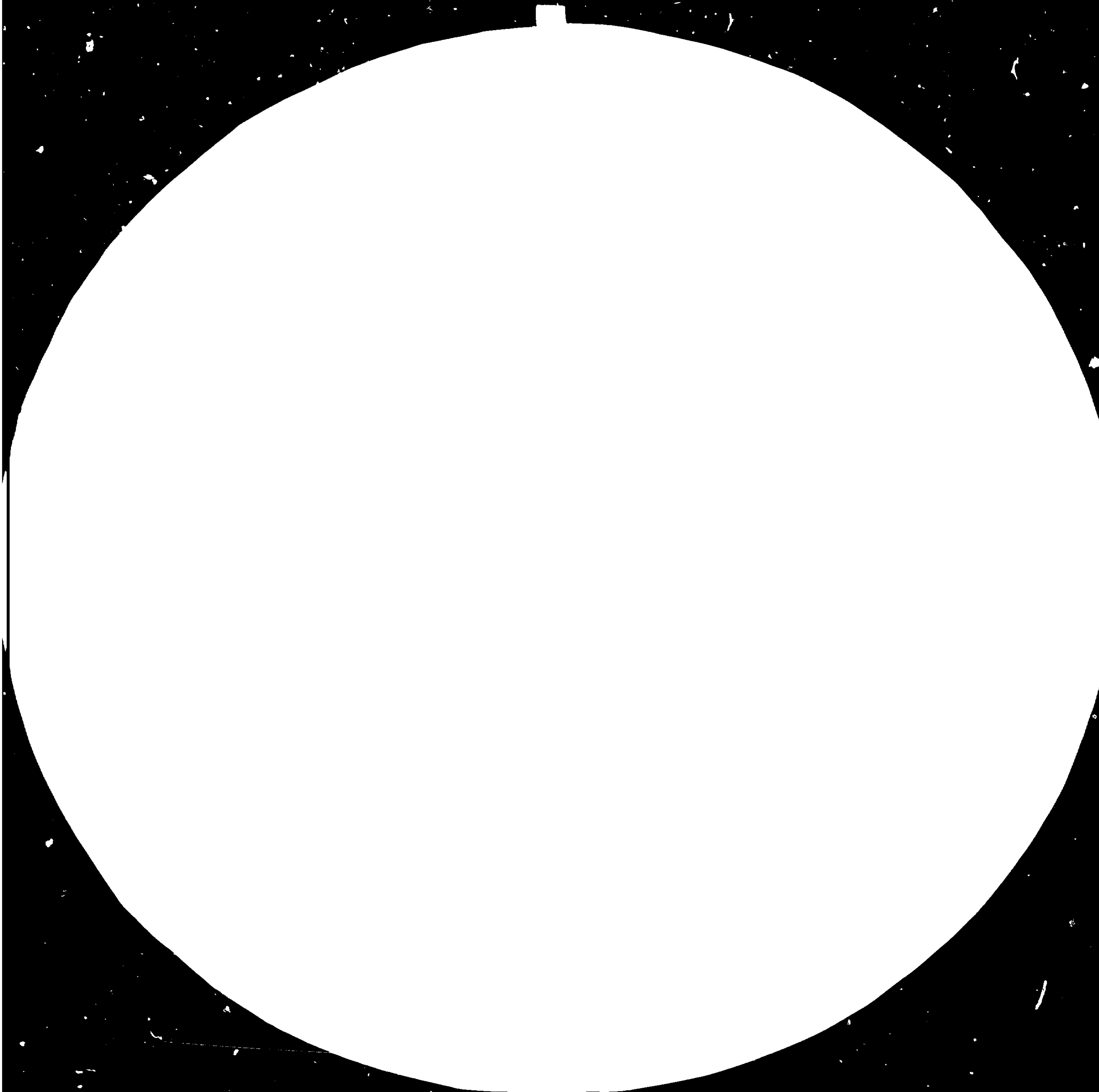

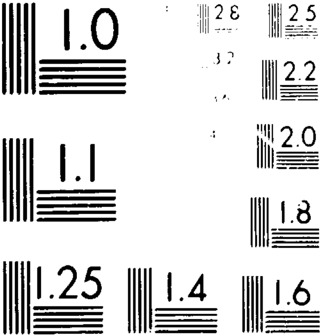

MICROCOPY RESOLUTION TEST CHART

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CALCULATIONS IN CERAMICS

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11

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Table of contents:

-...-

The UNIDO-Czechoslovakia Joint Programme in Pilsen is extending its assistance to developing and least developed countries in different directions with the aim to assist the governments in the development of industries based on indigenous materials. During its 5-year existence, the Joint Programme has met a lot of requests related to the transfer of technology and know-how. These requirements have been submitted by the trainees participating in a number of Technical Workshops organized in Pilsen and by experts stationed in the field.

The information on this process is transferred to developing and least developed countries by twinning arrangements with their technological institutes, individual training, group training, testing and evaluation of raw materials together with technological research and proposals of technologies, rendering advisory activities and extension of technical assistance in energy conservation. All these activities are connected with series of technological calculations, regarding dimensional changes, density, porous solids, suspensions, body calculations, glaze and fritted glaze calculations and calculations concerning heat transfer by conduction, convection and radiation.

The presented handbook comprises specific calculations applied in ceramic industries. Main principles of calculations are accompanied with practical examples so that they can be used not only for the manufacturing processes but also in laboratories, institutes, technical colleges and technical universities as teaching aid. It is the first summary publication embracing calculations related to all processes in the ceramic practice.

Z. A. Engelthaler
Chief Executive

Calculations in Ceramics may be divided into two main parts. Calculations concerning technology, properties of ceramic mass and products, and calculations concerning heat transfer.

A Technological calculations

During the many stages of processing, ceramic materials change in size, weight, composition, etc. These changes are often expressed in the form of percentages. There are three simple ideas involved in this procedure.

1. The change in a property is assessed by the difference between its final value and its initial value.
2. The fractional change in the property is given by the ratio:

$$\frac{\text{change in value}}{\text{initial value}} \qquad /1/$$

3. The percentage change in the property is defined as:

$$\frac{\text{change value}}{\text{initial value}} \times 100 \qquad /2/$$

i.e. Percentage change = Fractional Change x 100

I. Dimensional Changes

We recognize Drying, Firing and Total shrinkage.

a/ Drying Shrinkage or Wet-Dry contraction

During the drying of clayware the physically held moisture is removed and this is accompanied by a contraction of the product. In general, products having a high moisture content at the beginning of the drying process undergo high drying shrinkages. The process is normally carried out at temperatures up to 110°C.

The length of a product made from plastic clay was in wet state /before drying/ 20 cm, and in dry state /after drying/ 18,5 cm. The change in length is 1,5 cm and this may be expressed according to eq./2/ in percentage form as follows:

Percentage drying shrinkage $= \frac{1,5}{20} \cdot 100 = 7,5\ \%$.
This should be referred to as the linear drying shrinkage, since the measurements are taken along a single line.

In the laboratory, it is often convenient to mark a line of length, say 5 or 10 cm upon the trial piece whilst it is in the wet state. A further measurement, after drying, determines the wet-dry contraction.

Example

Length - wet state	100 mm
Length - dry state	92 mm
Change in length	8 mm

Percentage drying shrinkage $\frac{8}{100} \cdot 100 = 8\ \%$.

Another example

The diameter of a plate in the mould during plastic shaping is 25 cm. The drying shrinkage is 6 %; what will be the plate diameter after drying?

Change in length /along the diameter/ $= \frac{6}{100} \times 25 = 1,5$ cm.

Diameter after drying $= 25 - 1,5 = 23,5$ cm.

Suppose that the dried size and the percentage drying shrinkage are known. How may the initial size be calculated? A brick has a "dried length" $l_d = 16{,}1$ cm. The wet-dry contraction of the product is 5,8 %. What was the length l_p of the brick in the plastic state?

Let l_p represent the initial length of the brick, i.e. its length in the plastic state. Then, the change in length $= \frac{5{,}8}{100} \times l_p$ /cm/

$$\text{now} \quad l_p - \frac{5{,}8}{100} \cdot l_p = 16{,}1$$

$$\frac{94{,}2}{100} \cdot l_p = 16{,}1$$

$$l_p = 16{,}1 \times \frac{100}{94{,}2} = 17{,}1 \text{ /cm/}$$

b/ Firing Shrinkage /Dry-fired Contraction/

After drying, ceramic products are fired-usually to temperatures above 900°C. During this heat treatment, the melting of the more fusible components causes a further shrinkage of the product. This firing shrinkage is entirely dependent upon the composition of the mix and the firing schedule employed.

Calculations concerning this dry-fired contraction are similar to those already encountered during the drying process.

Example

The "Dried length" of a porcelain insulator is 6,53 cm.
After firing, its length becomes 6,18 cm.
Change in length = 0,35 cm
Percentage firing shrinkage $= \frac{0{,}35}{6{,}53} \times 100 = 5{,}36$ %.

c/ Total Shrinkage /Wet-fired Contraction/

The total shrinkage of a ceramic product takes into account the effects of both drying and firing.

Consider the marked length of a trial specimen of the various stages of processing:

Length /wet, plastic state/ ..l_p = 100 mm
Length /dry state/ ....l_d = 92 mm
Length /fired state/......... l_f = 88 mm
Total change in length ...... s_t = 12 mm

Percentage drying shrinkage

$$s_d = \frac{l_p - l_d}{l_p} \cdot 100 = \frac{100-92}{100} \cdot 100 = 8\ \% \qquad /3/$$

Percentage firing shrinkage

$$s_f = \frac{l_d - l_f}{l_d} \cdot 100 = \frac{92 - 88}{92} \cdot 100 = 4{,}35\ \% \qquad /4/$$

Percentage total shrinkage

$$s_t = \frac{l_p - l_f}{l_p} \cdot 100 = \frac{100 - 88}{100} \cdot 100 = 12\ \% \qquad /5/$$

The sum of the percentage drying shrinkage and percentage firing shrinkage is not equal to the percentage total shrinkage /since the percentage firing shrinkage is based upon l_d whereas the others are evaluated on a basis of l_p/.

Example

The required diameter of a finish product is 230 mm. If the firing contraction is 4,5 % and the drying contraction is 3,15 %,calculate the diameter after drying, the original mould diameter, and the percentage total contraction.

The dry-fired contraction is 4,5 %. Let D be the length of the diameter after drying. Then:

$$D - \frac{4,5}{100} D = 230 \qquad /6/$$

$$\frac{95,5}{100} D = 230$$

$$D = \frac{100}{95,5} \cdot 230 = 241 \text{ mm}$$

The diameter after drying is 241 mm. The wet-dry contraction is 3,15 %. Let M be the original mould diameter. Then

$$M - \frac{3,15}{100} M = 241 \qquad /7/$$

$$\frac{96,85}{100} M = 241$$

$$M = \frac{100}{96,85} \cdot 241 = 249 \text{ mm}$$

The original mould diameter is 249 mm
The total change in diameter is 249-230 = 19 mm
Percentage total shrinkage = $\frac{19}{230} \times 100 = 8,26$ %.

d/ Volume shrinkage

A more reliable assessment of shrinkage can sometimes be obtained, by considering changes in the volume of the clay product, at the various stages in its processing. Linear shrinkages may be different according to the dimension considered.

It may be noted, that the magnitude of a volume shrinkage is approximately three times the linear shrinkage of the same material. This fact may be demonstrated by considering a cube of the material, each side of which is "x" units of length, in the original state. Suppose that after processing, each side undergoes a change equal to "a" units of length. Then:

Percentage linear shrinkage $= \frac{a}{x} \times 100$

To find the percentage volume shrinkage:

Original volume $= x^3$ cubic units

Final volume $= /x-a/^3$ cubic units

$$\text{Percentage volume shrinkage} = \frac{x^3 - /x-a/^3}{x^3} \times 100$$

$$= \frac{x^3 - /x^3 - 3ax^2 + 3a^2x - a^3/}{x^3} \times 100$$

$$= \frac{3ax^2 - 3a^2x + a^3}{x^3} \times 100 = \left[\frac{3a}{x} - 3/\frac{a}{x}/^2 + /\frac{a}{x}/^3\right] \times 100 \qquad /8/$$

The quantity $\frac{a}{x}$ is small /"a" is much smaller than "x"/. Moreover, the quantities $/\frac{a}{x}/^2$ and $/\frac{a}{x}/^3$ must be very small indeed, and in an approximation these terms may be neglected. Hence:

Percentage volume shrinkage $\doteq$

$$\doteq \frac{3a}{x} \times 100 \qquad /9/$$

which is 3 times the value of the percentage linear shrinkage.

e/ Moisture content

The weight of physically-held water in a sample of raw material is an important factor in assessing its suitability for processing, or its actual composition or its economic value.

It is necessary to measure and control the moisture content of ceramic products at the various manufacturing stages. Moisture content is determined by the loss in weight of a sample of the material after drying at 110°C.

Percentage moisture content is

$$\frac{Lw}{Ww} \cdot 100 = M_w \ /\%/ \qquad /10/$$

or

$$\frac{Lw}{W_D} \cdot 100 = M_D \ /\%/ \qquad /11/$$

where L_w is the loss in weight of a sample after drying at 110°C

W_w is the weight of a sample in wet-plastic state

M_w is the percentage of moisture content on "wet" basis

M_D is the percentage of moisture content on "dry" basis

W_D is the weight of a sample in dry state

"Wet" or "Dry" basis for the expression of percentage moisture content

Example

A sample of china clay weighing 12,6 g is dried at 110°C to a constant weight of 10,8 g. What is its moisture content?

Loss in weight is 1,8 g

Percentage moisture content is in accordance with /10/

$$M_w = \frac{L_w}{W_w} \cdot 100 = \frac{1{,}8}{12{,}6} \times 100 = 14{,}28\ \%$$

The basis of this calculation is the initial weight of china clay i.e. the 'wet" weight . This is in accordance with the definition of percentage change as stated above. It is the commonly accepted basis for calculating percentage moisture content.

In some cases, however, it is convenient to calculate the percentage moisture content on a "dry" basis.

Consider a 250 g sample of plastic ball clay consisting of 200 g of dry clay and 50 g of water. Then according to /10/ resp. /11/

a/ Percentage moisture content
"Wet" basis

$$M_W = \frac{L_W}{W_W} \cdot 100 = \frac{50}{250} \times 100 = 20\ \%$$

b/ Percentage moisture content
"Dry" basis

$$M_D = \frac{L_W}{W_D} \cdot 100 = \frac{50}{200} \times 100 = 25\ \%$$

The numerical difference between the percentages is appreciable. It is important, therefore, that whenever the dry basis is used for the expression of percentage moisture contents, the fact must be stated.

<u>Example</u>

One hundredweight of plastic clay has a moisture content of 38 % /calculated on the "dry" basis/. Find the weights of water and dry clay involved in the mix, and calculate the percentage moisture content on the "wet" basis.

A 38 % moisture content /"dry" basis/ means that there is 38 parts by weight of water to every 100 parts by weight of dry clay. Hence:

In 500 g of plastic clay there is

$$\frac{38}{138} \times 500 = 137{,}7 \text{ g of water}$$

$$\text{and } \frac{100}{138} \times 500 = 362{,}3 \text{ g of dry clay}$$

Percentage moisture content /"wet" basis/ $= \frac{38}{138} \times 100 = 27{,}5$ %

f/ Relationship between percentage moisture content /dry basis/ and volume shrinkage

The changes both in size and weight of a material during the drying process may be illustrated on the same diagram. This method of presentation is often used to depict the drying characteristics of different types of clays.

Consider a sample of plastic clay consisting of 100 g of dry clay and 40 g of water. The percentage moisture content /dry basis/ is 40 %.

Suppose that the volume of the plastic clay is 80 cm^3 /point A on the diagram Fig.1/. Then in the early stages of drying, if the plastic clay loses 3 g of water, the percentage moisture content /dry basis/ will be reduced to 37 % and the volume of the plastic clay becomes 77 cm^3. There will be a simple relationship between the two properties, viz. the size of the plastic mass and the weight of water associated with it reduce by the same amounts, numerically. The point C, on the diagram, is of considerable importance. It is associated with :

a/ a moisture content /dry basis/ of 18 % at M. This is known as the CRITICAL MOISTURE CONTENT - which may be different with different types of clays. Below this value no further contraction takes place and drying may proceed more rapidly.

b/ a volume of 58 cm^3 which remains constant and is the final volume reached in the shrinkage process.

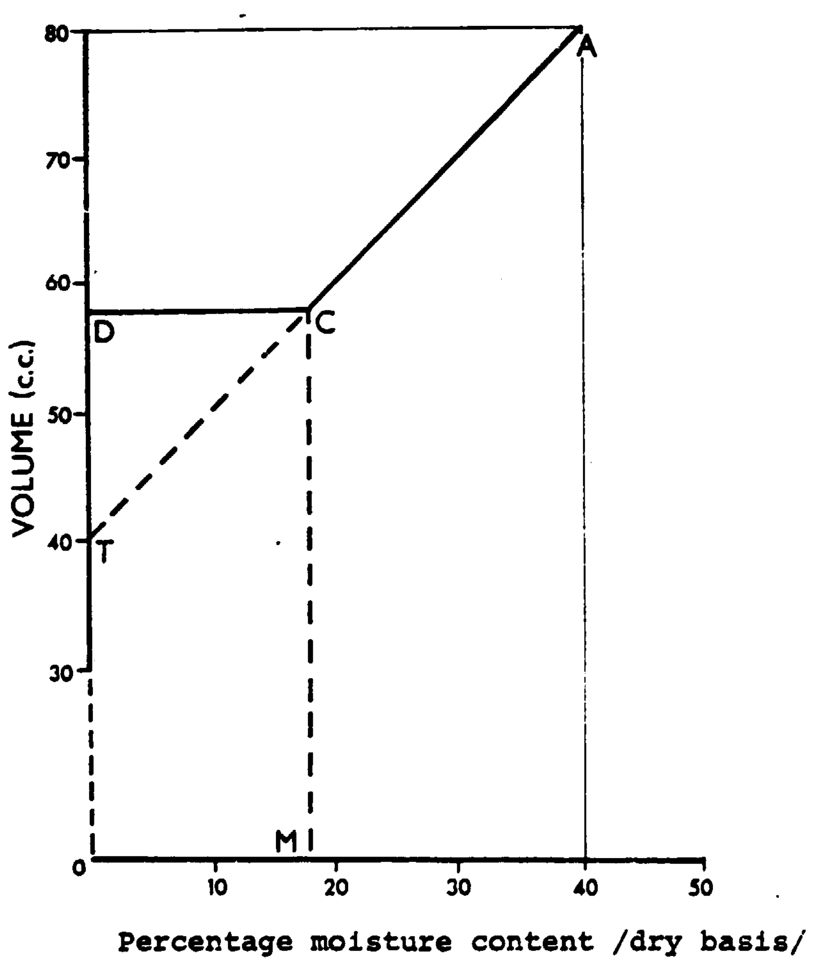

Fig.1 Drying characteristics

During the drying from C to D, no shrinkage occurs, since the solid particles are touching one another. The moisture in between the particles is gradually removed and the moisture content is reduced to zero at the point D.

The point T /reached by the extension of AC/ indicates the volume of the dry clay particles alone. It is the theoretical volume to which the clay would contract if the particles fitted together perfectly. /This volume may be used to calculate the TRUE DENSITY of the clay, i.e. $\frac{100g}{40cm^3}$ = = 2.50 g per cm^3/

The volume difference between D and T /i.e. 18cm^3/ represents the air space in the completely dried sample of clay- and hence indicates the "packing characteristics" of the material.

The diagram, therefore, provides a considerable amount of information concerning the physical properties of the clay. In particular, the shrinkage may be found for a drying operation between any required limits of moisture content.

Example

What contraction occurs if the clay is completely dried from a moisture content /dry basis/ of 32 %?

Original volume = 72 cm^3
Final volume = 58 cm^3
Percentage volume shrinkage = $\frac{14}{72}$ x 100 = 19,5 %

The percentage linear shrinkage will be approximately in acc. with /9/ $\frac{19.5}{3}$ = 6.5 %

g/Loss-on-Ignition

The chemical analysis of a ceramic material is usually determined on a sample which has been dried at 110°C, i.e. from which all physically-held water has been removed. To determine the loss-on-ignition, a known weight of the dried sample is heated to about 1,000°C and then reweighed.

The loss-on ignition, then, is the percentage loss in weight occuring over the temperature range 110-1,000°C. It is due to the loss of chemically combined water, to the combustion of carbonaceous materials, and to the breakdown of such compounds as calcium carbonate. It, therefore, corresponds to the weight loss of the material from the dry state to the fired state.

A sample of dried ball clay weighs 1.2869 g. After ignition its weight is 1.1682 g. What is the percentage loss-on-ignition?

$$\text{Percentage loss-on-ignition} = \frac{0.1187}{1.2869} \times 100 = 9.22\ \% \quad /12/$$

The percentage loss-on ignition, together with the percentage weights of SiO_2 Al_2O_3, CaO, and other "permanent" oxides, constitutes the chemical analysis of the material. In practice, the total of these percentage weights is seldom exactly 100.0 because of small inherent errors in the determination, and the difficulties involved in removing traces of reagents and in detecting minute amounts of impurities. /Totals between 99.5 and 100.5 are commonly accepted./

Suppose that the analysis of a material is reported as:

SiO_2 = 52.6 %
Al_2O_3 = 21,4 %
Loss-on-ignition = 9,3 %
Other "permanent" oxides = 16,7 %

If this material were fired it would then consist of:

SiO_2 = 52.6 parts by weight
Al_2O_3 = 21.4 parts by weight
Other oxides = 16.7 parts by weight
Total = 90.7 parts by weight

Converting this to percentage form:

$$SiO_2 = \frac{52.6}{90.7} \times 100 = 58.0\ \%$$

$$Al_2O_3 = \frac{21.4}{90.7} \times 100 = 23.6\ \%$$

$$\text{Other oxides} = \frac{16.7}{90.7} \times 100 = 18.4\ \%$$

$$\text{Total} = 100.0\ \%$$

Although the actual weight of silica /SiO_2/ remains unaltered during the firing, the fired material contains a greater proportion of silica than the dried material because of the loss-on ignition.

To reduce the percentage of defective ware, i advisable to test and control materials in the earlier stages of production. Hence, analytical data are often obtained on the unfired product and, by calculations, the properties of the final article may be predicted.

For adequate craze resistance a fired earthenware body is required to have a total silica content within the range 72-75 %. If a sample of unfired body has 67.8 % SiO_2 and a loss-on ignition of 7.3 %, will it satisfy the necessary requirement?

100 g unfired body → 92.7 g fired body
/containing 67.8 g SiO_2/ /containing 67.8 g SiO_2/

Percentage total silica /calculated on the fired body/ $= \frac{67.8}{92.7} \times 100 = 73.1\ \%$

Hence the requirement is met.

It is now possible to predict the final analysis of the fired product if sufficient information is given concerning the body components. To illustrate this, consider the following example:

A body recipe is: Ball clay, 25; china clay, 25; flint, 35; stone, 15.

Analytical data:

	Ball clay	China clay	Flint	Stone
SiO_2	48.4 %	47.3 %	98.5 %	71.6 %
Loss-on ignition	11.5 %	12.1 %	0.2 %	1.2 %

Calculate the percentage total silica in the fired body.

	Dry weight	Fired weight	Weight of silica in fired material*
Ball clay	25	$\frac{88.5}{100} \times 25 = 22.1$	$\frac{48.4}{100} \times 25 = 12.1$
China clay	25	$\frac{87.9}{100} \times 25 = 22.0$	$\frac{47.3}{100} \times 25 = 11.8$
Flint	35	$\frac{99.8}{100} \times 35 = 34.9$	$\frac{98.5}{100} \times 35 = 34.5$
Stone	15	$\frac{98.8}{100} \times 15 = 14.8$	$\frac{71.6}{100} \times 15 = 10.7$
		Total 93.8	69.1

* The actual weight of silica in the fired material is the same as that in the unfired material.

Hence 93.8 units of weight of fired body contain 69.1 units of weight of silica

$$\text{Percentage total silica /calculated on the fired body/} = \frac{69.1}{93.8} \times 100 = 73.7 \quad /13/$$

h/ Problems

1.
A test piece of bone china body has a "marked" length of 5.0 cm in the plastic state. After drying, the distance between the marks is 4.80 cm and after firing 4.35 cm. Calculate the percentage drying shrinkage the percentage firing shrinkage, and the percentage total shrinkage.

According to /3/, /4/, and /5/ we may proceed as follows:

length in wet, plastic state $l_p = 5{,}0$ cm
length in dry state $l_d = 4{,}8$ cm
length in fired state $l_f = 4{,}35$ cm

Percentage drying shrinkage according to /3/:

$$s_d = \frac{l_p - l_d}{l_p} \cdot 100 = \frac{5 - 4{,}8}{5} \cdot 100 = 4\ \%$$

Percentage firing shrinkage - eq. /4/:

$$s_f = \frac{l_d - l_f}{l_d} \cdot 100 = \frac{4{,}8 - 4{,}35}{4{,}8} \cdot 100 = 9{,}375\ \%$$

Percentage total shrinkage - eq./5/

$$s_t = \frac{l_p - l_f}{l_p} \cdot 100 = \frac{5 - 4{,}35}{5} \cdot 100 = 13\ \%$$

2.
A product has a fired length of 235 mm, a drying shrinkage of 5.6 % and a firing shrinkage of 8.5 %.

Calculate a the "wet" length, b the "dry" length, and c the percentage total concentration. We shall apply the equations /6/ and /7/ calculate the D /or l_d/ and M /l_p/:

$$D - \frac{8,5}{100} D = 235$$

$$\frac{91,5}{100} D = 235$$

$$D = \frac{100}{91,5} . 235 = 257 \text{ mm}$$

The dry length l_d /MD/ is 257 mm

The wet length according /7/ will be:

$$M - \frac{5,6}{100} . M = D$$

$$M - \frac{5,6}{100} . M = 257$$

$$M = \frac{100}{94,4} . 257 = 272 \text{ mm}$$

a/The wet length l_p /or M/ is 272 mm. Percentage total concentration according to /5/

$$s_t = \frac{272-235}{272} . 100 = \frac{37}{272} . 100 = 13,6 \%$$

3. The "die" size of a brick is 31x15x7 cm. If the total volume shrinkage is 21,5%, what is a/ the volume, and b/ the approximate length of the fired brick ?

The "die" i.e. the plastic /wet/ volume is

$$V_p = 31 \times 15 \times 7 = 3255 \text{ cm}^3$$

The fired volume will be

a/ $$V_f = V_p - \frac{21,5}{100} . V_p = 3255 - 700 = 2555 \text{ cm}^3 \doteq 2,6 \text{ dm}^3$$

b/ Percentage total length shrinkage according to / 9 /

$$s_t \doteq \frac{s_v}{3} = \frac{21,5}{3} \doteq 7,2\ \%$$

where s_v is the percentage volume shrinkage.

The approximate length of the brick will be:

$$l_f = l_p - \frac{7,2}{100} \cdot l_p = \frac{92,8}{100} \cdot l_p$$

$$l_f = \frac{92,8}{100} \cdot 31 = 28,8\ \text{cm}$$

4.

A partially dried product has a moisture content of 6.0%. If $4\frac{1}{2}$ tons of such product are now dried completely, what weight of physically-held water is liberated?

According to / 10 /

$$M_w = \frac{L_w}{W_w} \cdot 100 \quad ; \quad M_w = 6\% \quad ; \quad W_w = 4500\ \text{kg}$$

$$6 = \frac{L_w}{4500} \times 100 \quad ; \qquad L_w = 270\ \text{kg}$$

Weight of liberated water is 270 kg.

5.

The "dry" recipe of a bone china body is: Bone 50; China clay 25; Stone 25. If the raw materials have moisture contents of 4,2%, 8,1% and 2,5% respectively, what actual weights should be used to make 100 kg of dry body?

Solution:

Bone:

50 kg of raw material with 4,2% moisture content has
95,8% dry material

x kg of raw material with 0% moisture content has
100 % dry material

therefore $x : 50 = 100 : 95,8$

$$x = \frac{50 \times 100}{95,8} = \underline{52,2 \text{ kg}}$$

China clay:

25 kg	8,1% moisture	91,9% dry mat.
x kg	0 % -"-	100 % -"- -"-

$$x = \frac{25 \times 100}{91,9} = \underline{27,2 \text{ kg}}$$

Stone:

25 kg	2,5% moisture	97,5% dry mat.
x kg	0 % -"-	100 % -"- -"-

$$x = \frac{25 \times 100}{97,5} = \underline{25,64 \text{ kg}}$$

6.

Four tons of plastic clay has a moisture content of 45,0% /dry basis/. Calculate a/ the weight of dry clay, b/ the weight of water, and c/ the percentage moisture content /wet basis/.

According to /11/

$$\frac{L_W}{W_D} \cdot 100 = M_D$$

where L_W is the weight of water
W_D is the weight of dry clay
M_D is the percentage of moisture content on "dry" basis i.e. 45%

We do not know L_w and W_D, but we know that

$$L_w + W_D = 4000 \text{ kg} \quad /4 \text{ tons of plastic clay}/$$

therefore

$L_w = 4000 - W_D$ will be inserted into /11/

$$\frac{4000 - W_D}{W_D} \cdot 100 = M_D$$

$$(4000 - W_D) \cdot 100 = 45 \times W_D$$

$$145\ W_D = 400000$$

$W_D = 2758,6$ kg is the weight of dry clay.

The weight of water is 1241,4 kg which is 31% /wet basis/.

7.

What weights of dry clay and water must be mixed to yield 2 kg of plastic clay having a moisture content of 48,0% /dry basis/ ?

The calculation will be similar as in the example number 6. We shall use again the eq./11/

$$\frac{L_w}{W_D} \cdot 100 = M_D \quad ; \quad L_w + W_D = 2000 \text{ g}$$

$$L_w = 2000 - W_D$$

$$\frac{2000 - W_D}{W_D} \cdot 100 = 48$$

$$148\ W_D = 200000$$

$W_D = 1351,4$ g dry **clay**

Weight of water will be 648,6 g which is 32,4% on wet basis.

8.

5.0 g of plastic clay after drying at 110°C weigh 4,216 g. When fired at 1.100°C, the weight becomes 3,927 g. Calculate a the percentage moisture content, and b the percentage loss-on-ignition. According to eq. /10/ the percentage moisture content is

$$M_w = \frac{5-4,216}{5} \cdot 100 = \frac{0,784}{5} \cdot 100 = \underline{15,7\ \%}$$

The percentage of moisture content is 15,7%.

According to eq. /12/ the percentage loss-on-ignition is

$$\frac{4,216 - 3,927}{4,216} \cdot 100 = \frac{0,289}{4,216} \cdot 100 = \underline{6,85\ \%}$$

The percentage loss-on-ignition is 6,85%.

9.

A partial analysis on a sample of unfired earthenware body shows 68,42% SiO_2 and a loss-on-ignition of 7,18%. Calculate the percentage silica in the fired body.

The analysis od the material is:

SiO_2	68,42
loss-on-ignition	7,18
other oxides	24,40
total	100.-

According to eq. /13/

percentage total silica $\frac{68,42}{92,8} \cdot 100 = 73,7\ \%$

Percentage total silica in the fired body is 73,7%.

II. Density

Density $\rho\,[kg\ m^{-3}]$ is a property of substances which is determined by the composition of the substance, does not depend on the place of measurement, but depend on the physical conditions, e.g. according to the relationship

$$\rho = \rho_n(1 - \mathcal{H}\Delta p)(1 - \gamma T) \qquad /14/$$

where ρ_n = normal density ascertained under normal pressure,

$p_n = 1{,}01325.10^5\,[Nm^{-2}]$ and at normal temperature

$T_n = 0^oC$

$\mathcal{H}$ = compressibility,

$\Delta p = p - p_n$, departure from standard pressure

γ = the volume thermal expansion

and T = temperature ^oC

In the study of the physical properties of a ceramic material, a knowledge of its density is of fundamental importance. The density of a body is defined by the relationship between its mass and its volume.

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}} \qquad /15/$$

The mass of a body is the amount of matter in it, and it is measured by comparing its gravity pull /weight/ with that of standard masses /boxes of weights/. For routine work in factories and laboratories, the mass of a body is numerically the same as its weight:

e.g. An object weighing 16,4 kg has a mass of 16,4 kg

The basic SI unit of mass is 1 kg.

g, mg, μg and t are permited, although t will normally be used for 1000 kg instead of Mg.

The volume of a body is a measure of its "over-all" size, i.e. the amount of space it occupies.

The main basic SI unit of volume is 1 m^3. Permited are 0,001 m^3 which is 1 dm^3 or 1 l and 0,000001 m^3 which is 1 cm^3 or 1 ml. The basic SI unit of density is 1 kg m^{-3}. Used and permited are 1 kg dm^{-3}, 1 g cm^{-3} and 1 t m^{-3} which all are equal 1000 kg m^{-3}.

Examples:

1/ If 100 g of mercury occupy a volume of 7,35 cm^3 then the density of mercury $= \frac{\text{Mass}}{\text{Volume}} = \frac{100\ g}{7{,}35 cm^3}$

$= 13{,}6\ g\ cm^{-3}$

2/ A piece of glass weighs 14,26 g and has a volume of 5,8 cm^3. What is its density ?

Density of glass $= \frac{14{,}26\ g}{5{,}8\ cm^3} = 2{,}46\ g\ cm^{-3}$

3/ A 50 ml bottle filled with a salt solution weighs 95,286 g. The weight of the bottle is 42,341 g. What is the density of the salt solution?

50 ml of salt solution weigh 52,945 g. Density of salt solution $= \frac{52{,}945}{50} = \underline{1{,}059\ g\ cm^{-3}}$

4/ A vitreous brick has a density of 2,54 g cm^{-3} and weight 2,5 kg ? What is its volume in cm^3 ?

Density $= \frac{\text{Weight}}{\text{Volume}}$

$$\text{Volume} = \frac{\text{Weight}}{\text{Density}} = \frac{2500\ \text{g}}{2{,}54\ \text{gcm}^{-3}} = 984{,}25\ \text{cm}^3$$

Archimedes Principle

In measuring the density of solid bodies it is convenient to use Archimedes' Principle which states that:

When a body is immersed in a fluid, its apparent loss in weight /upthrust/ is equal to the weight of fluid displaced.

With conventional laboratory equipment the volume of a solid material cannot be measured accurately, whereas weighings can be made with greater precision. The application of Archimedes' Principle avoids the direct measurement of the volume of the solid body.

If D = the "dry" weight /i.e. in air/ of the body; and

I = the weight of the body when immersed in water /density of which is 1 gcm^{-3}/ - often called suspended weight; then

D - I = the numerical value of weight of water /in g/ having the same numerical value of volume /in cm^3/ as the body.

Hence, density of the body = $\frac{D}{D-I}$ $[\text{g cm}^{-3}]$.

Example.

A solid piece of metal weighs 24,63 g in air and 19,86 g when immersed in water. What is its numerical value of density?

$$\text{Density of metal} = \frac{\text{Weight of metal}}{\text{Weight of same volume of water}} =$$

$$= \frac{D}{D-1}$$

$$= \frac{24,63}{24,63-19,86} = 5,16 \quad gcm^{-3}$$

If a liquid other than water is used in determining the volume of the test material, then the density of the liquid itself must be taken into account.

Example: A test piece weighs 20,42 g. When immersed in paraffin /of density 0,813 g per cm^3/ its weight is 15,37 g. What is the density of the test material?

By Archimedes' Principle, the apparent loss in weight /5,05 g/ is equal to the weight of paraffin displaced.

Now, since $\quad \text{Volume} = \frac{\text{Weight}}{\text{Density}}$

$$\text{the volume of paraffin displaced} = \frac{5,05}{0,813} =$$

$$= 6,21 \ cm^3$$

and this is also the volume of the test piece.

Hence, $\quad \text{Density of the test material} = \frac{20,42}{6,21} =$

$$= 3,29 \ gcm^{-3}$$

The materials so far considered have been simple, uniform substances, existing in only one physical state, i.e. entirely as a solid or entirely as a liquid.

Many ceramic materials are more complex, since they are often mixtures of components which have different physical states. The two main categories are:

1/ Porous Solids - composed of solid material interspersed with pore spaces, e.g. a fired earthenware body; a plaster mould.

2/ Suspensions - consisting of solid particles in a liquid medium /usually water/, e.g. a casting slip; a glaze suspension.

Values of mass, volume and density of several substances are in the following Table I.

Table I.

Material	Weight/mass/	Volume	Density
Glass	41,66 g	16,8 cm^3	2,48 gcm^{-3}
Paraffin	39,2 g	50.- cm^3	0,784 gcm^{-3}
Alumina	84,3 g	22,48 cm^3	3,75 gcm^{-3}
Kaolin	156,0 g	62,4 cm^3	2,5 gcm^{-3}
Steel.	1,0 t	0,129 m^3	7760.- kgm^{-3}

Example:

A vessel weighing 48,6 g is completely filled with a liquid of density 1,575 gcm^{-3}. If the gross weight is then 216,3 g what is the capacity of the vessel - in cm^3.

The weight of the liquid is 216,3 - 48,6 - 167,7 g.

The capacity of the vessel will be then

$$\frac{167,7}{1,575} - 106,5\ cm^3$$

III. Porous Solids

Effect of Porosity on the Function of Ceramic Materials.

The amount of pore space in a ceramic material has far-reaching effects on its properties.

A dense, non-porous material tends to dunt far more readily than a porous one, since the latter is capable of relieving stresses within the pore structure.

Highly porous materials should not be used where there is a risk of corrosion, since the cavities provide centres of attack and a large overall surface area. Similarly, such materials have a low resistance to erosion and abrasion.

In general terms, ware with high porosity has less mechanical strength than a similar vitreous product.

Porosity plays an important role in the drying rates of clay goods. As might be expected, an open porous body can be dried rapidly. In the heavy clay industries highly plastic clays, which form closepacked. dense bodies,are difficult to dry at an economical rate. For this reason, many clays have to be heavily grogged, so that, without cracking or distorting, they can be dried more quickly.

The amount of air phase present influences thermal conductivity. Materials with high porosity are generally good heat insulators and also have low electrical conductivity.

The viscosity and density of a glaze suspension may need adjustment according to the porosity of the ware, in order to regulate the "pick-up" of glaze.

The vitrification characteristics of a ceramic material are often illustrated by a diagram showing the porosity of the material at many different firing temperatures.

Pore Structure

Most ceramic products can be classed as porous solids, in which the continuity of the solid matter is interrupted by voids of different kinds.

In general there are two main types of pores: open and sealed pores. Open pores are voids which are accessible /at the surface of the article/ to penetration by a fluid. They exist because of the imperfect packing of the individual particles of the material and also to the escape of gases during drying and firing processes.

Sealed pores are formed on firing when bubbles of gas are frozen into the glassy matrix, or when open pores are sealed by molten material.

Some clays and bodies "bloat" when overfired. This is due to the melting action of the fluxes, together with the evolution of gases from such impurities as calcium sulphate. Large numbers of bubbles and blisters are formed, and the article expands, becoming a mass of sealed pores as the bloating continues.

Density of Porous Solids

The density of a material has been defined as a relationship between its mass /weight/ and its volume.

For a vitreous object there is only one weight and one volume involved.

For a porous solid, however, there are different ways of expressing its volume, and these must be defined before any precise meaning can be given to its density.

There are three volume expressions in common use:

1. Apparent Volume

This is the "envelope" volume of the porous solid /sometimes referred to as the Bulk Volume/, and includes the volume of the solid component, open pores and sealed pores.

It may be determined by:

a/ Physical measurements of the test piece in suitable cases, e.g. a porous brick of sides 29 x 14 x 6,5 cm has an apparent volume of 2639 cm^3.

b/ Using a mercury displacement method, e.g. a volumeter /the mercury does not enter the small open pores/.

c/ The difference between the soaked weight /S/ and the immersed weight /I/ of the piece. If water is used as the fluid medium, then the numerical value of /S-I/ g gives the apparent volume in cm^3.

2. True Volume

This refers to the volume of the solid component only. It may be determined by crushing the piece into powder form- so that all the pores are destroyed - and then using a "density bottle" method.

3. Apparent-solid Volume

This volume lies in between 1 and 2 . It is the volume of the solid component and sealed pores only, and is obtained from the difference between the dry weight D and the immersed weight I of the piece.

S-I gives the volume of open pores+sealed pores+solid /17/

S-D gives the volume of open pores /18/

and by substraction

D-I gives the volume of sealed pores+solid /19/

A piece of porous material has only one weight /since the weight of air in the pore system may be neglected/. Consequently there are three expressions of density, corresponding to the three volume expressions defined above.

$$\text{Apparent/or bulk/density} = \frac{\text{Weight}}{\text{Apparent volume}} \qquad /20/$$

$$\text{True density} = \frac{\text{Weight}}{\text{True volume}} \qquad /21/$$

$$\text{Apparent solid-density} = \frac{\text{Weight}}{\text{Apparent-solid volume}} \qquad /22/$$

For all density expressions, the units employed must be clearly stated as kg per m^3; g per cm^3; kg per dm^3 etc.

<u>Example</u>

A porous ceramic test piece has weight /dry/= 14,62 g ; weight soaked = 16,25 g ; and weight immersed = 8,37 g. Calculate

a/ its apparent density; b/ its apparent-solid density.

According to /20/

a/ the apparent density $= \frac{D}{S-I} = \frac{14,62}{7,88} = 1,85$ g per cm^3

According to /22/

b/ the apparent-solid density $= \frac{D}{D-I} = \frac{14,62}{6,25} = 2,34$ gcm^{-3}

Porosity

This property is measured by comparing the volume of the pores with the dimensions of the piece itself.

Once again, it is important to define clearly what is meant by "pores" and whether the test piece is to be measured in terms of weight or volume.

The two most widely used expressions are Apparent Porosity and Water Absorption.

Apparent porosity is the ratio of open volume to total volume. Hence:

$$\text{Percentage apparent porosity} = \frac{\text{Open pore volume}}{\text{Total volume}} \times 100$$

$$= \frac{S-D}{S-I} \times 100 \qquad /23/$$

Water absorption is the ratio of open pore volume to the weight of the test piece. Therefore:

$$\text{Percentage water absorption} = \frac{\text{Open pore volume}}{\text{Weight}} \times 100$$

$$= \frac{S-D}{D} \times 100 \qquad /24/$$

The determination of water absorption is often used for "works control" purposes because it is simpler and less time-consuming than the measurement of apparent porosity /the immersed weight of the piece is not required in the water-absorption test/.

The difference between absorption per unit volume /apparent porosity/ and absorption per unit weight /water absorption/ is illustrated in the following example:

A trial piece weighs 210 g; after soaking in water it weighs 250 g; and when suspended in water its weight is 150 g. Calculate the percentage apparent porosity and the percentage water absorption.

According to /23/

$$\text{the percentage apparent porosity} = \frac{S-D}{S-I} \times 100 = \frac{250-210}{250-150} \times 100 =$$

$$= 40{,}0\ \%$$

In accordance with /24/

$$\text{the percentage water absorption} = \frac{S-D}{D} \times 100 = \frac{250-210}{210} \times 100 =$$

$$= 19\ \%$$

For most ceramic materials, the apparent porosity is approximately twice the value of the water absorption.

Apparent porosity measurements provide a better basis for the comparison of ceramic materials in general-the value of the "open pores per unit volume" is directly related to such properties as glaze "pick-up", and, upon this basis, the ceramist may make a fair comparison between porous materials of different bulk densities, e.g. an earthenware body and a high-alumina body.

Determination of Apparent Porosity

Most laboratories use paraffin, rather than water, since it has better penetrating properties and a lower rate of evaporation.

The same formula for apparent porosity is used, i.e. /23/

$$\text{Percentage apparent porosity} = \frac{S-D}{S-I} \times 100$$

where D = weight of dry test piece;

S = weight of test piece after soaking in paraffin;

I = weight of immersed test piece /suspended in paraffin/.

In fact, the apparent porosity formula applies whatever liquid is used, since the ratio

$$\frac{\text{Weight of liquid filling the open pores}}{\text{Weight of liquid having the same apparent volume as the test piece}}$$

remains the same.

/For the determination of the density of a ceramic material the density of any liquid used in the measuring process must be taken into account/. See Chapter II, and the remark on p. 24

True Porosity

For the complete assessment of the porosity of a material all the pores /open and sealed/ must be considered. In this case the true porosity of the material is determined:

$$\text{Percentage true porosity} = \frac{\text{Volume of all pores}}{\text{Total volume of the test piece}} \times 100$$

$$= \frac{\text{Apparent volume} - \text{True volume}}{\text{Apparent volume}} \times 100$$

$$= \left(1 - \frac{\text{True volume}}{\text{Apparent volume}}\right) \times 100 \qquad /25/$$

$$\frac{\text{True volume}}{\text{Apparent volume}} = \frac{\frac{\text{Weight}}{D_t}}{\frac{\text{Weight}}{D_a}} = \frac{D_a}{D_t} \qquad /26/$$

$$\text{Percentage true porosity } [\%] = \left(1 - \frac{D_a}{D_t}\right) \times 100\ [\%] \qquad /27/$$

where

$$D_a = \text{Apparent density} = \frac{\text{Weight}}{\text{Apparent volume}} \qquad /28/$$

$$D_t = \text{True density} = \frac{\text{Weight}}{\text{True volume}} \qquad /29/$$

It is evident that the determination of true porosity involves a knowledge of the true density of the material. This latter property of the material can only be assessed by using a sample which has been crushed into fine powder form, i.e. in which all the pore system has been destroyed.

Sealed Pores

The volume of sealed pores in the material is obtained by difference:

$$\text{Percentage sealed pores} = \text{Percentage true porosity} - \text{Percentage apparent porosity}$$

Examples:

1/ A brick 29x14x6,5 weighs 4,5 kg. If the true density is 2,8 gcm^{-3}, calculate the percentage true porosity.

According to /27/ the percentage true porosity is

$$t_p \,\% = \left(1 - \frac{D_a}{D_t} \right) \times 100$$

Apparent density acc.to /28/:

$$D_a = \frac{\text{weight}}{\text{app.volume}} = \frac{4500 \text{ g}}{29 \times 14 \times 6{,}5 \text{ cm}^3} = \frac{4500}{2639} = 1{,}705 \text{ gcm}^{-3}$$

True Density $D_t = 2{,}8 \text{ gcm}^{-3}$

$$t_p \,\% = \left(1 - \frac{D_a}{D_t}\right) .\, 100 = \left(1 - \frac{1{,}705}{2{,}8}\right) .\, 100 = 39 \,\%$$

2/ The external dimensions of a porous test piece are 10x10x5 cm. The weight in air is 1,300 g ; after soaking in water, it weighs 1,410 g. Calculate the bulk density and percentage apparent porosity of the material.

According to /20/

$$\text{the Bulk density} = \frac{\text{Weight}}{\text{Apparent volume}}$$

$$= \frac{1{,}300}{10 \times 10 \times 5} = 2{,}6 \text{ g per cm}^3$$

According to /23/

the Percentage apparent porosity =

$$= \frac{\text{Volume of open pores}}{\text{Apparent volume}} \times 100 = \frac{S - D}{\text{Apparent volume}} \times 100 =$$

$$= \frac{110}{10 \times 10 \times 5} \times 100 = 22 \,\%$$

Problems

1/ Calculate /a/ the bulk density, and /b/ the percentage apparent porosity, of the test pieces from the following data:

	/A/	/B/	
Weight dry /g/	120	92	... D
Weight soaked in water/g/	146	105	... S
Weight suspended in water/g/	72	43	... I

The weight of the test piece after soaking in water is S. The weight of the test piece suspended /immersed/ in water is I.

According to Archimedes Principle an apparent loss in weight /upthrust/ of a body immersed in a fluid is equal to the weight of fluid displaced. In case the fluid is water having density of 1 gcm^{-3} then the apparent loss in weight in g equals the apparent /bulk/ volume of the test piece in cm^3.

a/ The bulk /apparent/ volume will be then S-I /see /17// and the bulk density $= \frac{D}{S-I}$ ... see eq. /20/

A. $\frac{120}{146-72} = \frac{120}{74} = 1,62\ gcm^{-3}$

B. $\frac{92}{105-43} = \frac{92}{62} = 1,48\ gcm^{-3}$

b/ According to /23/ the percentage apparent porosity will be:

A. $\frac{146-120}{146-72} \cdot 100 = \frac{26}{74} \cdot 100 = 35{,}1\ \%$

B. $\frac{105-92}{105-43} \cdot 100 = \frac{13}{62} \cdot 100 = 21\ \%$

2/ Calculate /a/ the percentage apparent porosity, /b/ the percentage water absorption, and /c/ the apparent-solid density, of a trial brick, given that:

Weight dry = 280 g .... D
Weight soaked in water= 342 g .... S
Weight suspended in water= 149 g I

a/ According to /23/ the percentage apparent

$$\text{porosity} = \frac{S-D}{S-I} \cdot 100$$

i.e. $\frac{342-280}{342-149} \cdot 100 = \frac{62}{193} \cdot 100 = 32{,}1\ \%$

b/ According to eq. /24/ the percentage water

$$\text{absorption} = \frac{S-D}{D} \cdot 100$$

i.e. $\frac{342-280}{280} \cdot 100 = \frac{62}{280} \cdot 100 = 22{,}1\ \%$

c/ According to /22/ Apparent-solid density =

$$= \frac{\text{Weight}}{\text{Apparent-solid volume}}$$

Apparent-solid volume is the difference between the dry weight /D/ and the immersed weight /I/ of the piece /see eq./19//. In accordance with /22/ the Apparent-solid density =

$$= \frac{280}{280-149} = \frac{280}{131} = 2{,}14\ \text{gcm}^{-3}$$

3/ A test-piece weighs 84,1 g in air and 47,3 g when immersed in water. If the percentage apparent porosity is 23,6% calculate the bulk density.

84,1 g ...... D

47,3 g I

According to /23/ the percentage apparent porosity $= \frac{S-D}{S-I} . 100$

$$23,6\ S - 23,6\ I = 100\ S - 100\ D$$

$$76,4\ S = 100\ D - 23,6\ I$$

$$S = \frac{100\ D - 23,6\ I}{76,4} = \frac{100 \times 84,1 - 23,6 \times 47,3}{76,4} = \frac{7293,7}{76,4} = 95,46\ g$$

Acc./17/ the Apparent /bulk/ volume $= S-I = 95,46-47,3 =$

$= 48,16\ cm^3$

Acc./20/ the Apparent /bulk/ density $= \frac{\text{Weight}}{\text{Appar.volume}} = \frac{84,1}{48,16} =$

$= 1,75\ gcm^{-3}$

4/ The dimensions of a trial silica brick are 4 cmx4 cmx2 cm, and the true density is 2,39 gcm^{-3}. If its weight /dry/ is 72 g calculate the percentage true porosity.

True density $D_t = 2,39\ gcm^{-3}$

$D_t = \frac{\text{Weight}}{\text{True volume}}$ ..... see eq./29/

Acc. /28/ the Apparent density $D_a = \frac{\text{Weight}}{\text{Apparent volume}} = \frac{72}{4x4x2} =$

$= 2.25\ gcm^{-3}$

According to /27/ the true porosity /%/ $= \left(1- \frac{D_a}{D_t}\right). 100 =$

$= \left(1- \frac{2,25}{2,39}\right). 100 = \underline{5,86\ \%}$

5/ A sample of flint-density = 2,63 gcm^{-3} is heated to 1450 °C; after calcination, the density is 2,34 gcm^{-3}. What is the percentage increase in volume of the original flint sample?

The lower the density the higher the volume:

$$\begin{array}{c l r c} \downarrow & 2,63\ gcm^{-3} \ \ldots\ldots\ldots\ldots & 100\ \% & \uparrow \\ & 2,34\ gcm^{-3} \ \ldots\ldots\ldots\ldots & x\ \% & \\ \hline \end{array}$$

$$x = \frac{100x2,63}{2,34} = 112,39\ \%$$

The percentage increase in volume is 12,4 %.

6/ The apparent density of a brick is 1,7 gcm^{-3} and the true density 2,4 gcm^{-3}. If a test piece has dimensions 3x4x2 cm^3, calculate the weight of water it may absorb/assuming no sealed pores/

$$D_a = 1,7\ gcm^{-3} \quad ; \qquad D_t = 2,4\ gcm^{-3}$$

According to /27/ the percentage true porosity $= \left(1- \frac{D_a}{D_t}\right).100$

$$\left(1- \frac{1,7}{2,4}\right).100 = 29,2\ \%$$

The test piece volume is 3x4x2 = 24 cm^3

The weight of water which may be absorbed will be 24x0,292 = <u>7 g</u>

7/ A porous test piece weighs 47,3 g and displaces 312 g of mercury from a volumeter. What is the bulk density of the material? /Density of mercury is 13,6 g per cm^3/

The volume of displaced mercury is

$$\frac{312}{13,6} = 22,94\ cm^3$$

The bulk density of the material - according to /28/ - will be then

$$\frac{\text{Weight}}{\text{Apparent volume}} = \frac{47,3}{22,94} = \underline{2,06\ gcm^{-3}}$$

IV. Suspensions

In the ceramic industry, a suspension of solid particles in a fluid is often referred to as a Slip. The solid component may be clay, flint, quartz, stone, felspar, glaze, colour, etc., and the liquid component is usually water.

In most laboratories, the metric system is used for the measurement of weights and volumes. It is convenient, therefore, to weigh 200 cc of the slip /using a 250 ml measuring cylinder/.

E.g. If 200 cm^3 of the slip weighs = 326 g

then the density of the slip $= \frac{326 \text{ g}}{200 \text{ cm}^3} = 1{,}63$ g per cm^3

Consider a slip made from solid particles of stone /density 2,6 gcm^{-3}/ and water /density 1 gcm^{-3}/. What are the maximum and minimum density limits of all the possible slips that could be made from these two components?

Clearly the maximum density slip is obtained in the theoretical case when it consists of a solid block of stone /no water at all/, and the density would be 2,60 gcm^{-3}.

The minimum density slip would be entirely water /no stone particles/ and hence its density would be 1 gcm^{-3}.

It specified amounts of water and powdered material are mixed, what will be the density of resultant slip?

This type of problem may be solved using the relationship

$$\text{Density} = \frac{\text{Weight}}{\text{Volume}} \qquad /15/$$

Then

$$\text{Density of slip} = \frac{\text{Total weight of components}}{\text{Total volume of components}} \qquad /30/$$

Example

1/ In the laboratory a suspension is made using 20 g of dry clay /density = 2,62/ and 30 cm^3 of water. What is its density in gcm^{-3}?

Material	Weight /g/	Volume /cm^3/	Density /gcm^{-3}/
a/ Dry clay	20	/7,63/	2,62
b/ Water	/30/	30,0	1,00
c/ Slip	/50/	/37,63/	/1,33/

a/ 20 g of dry clay would occupy a volume of $\frac{20}{2.62} = 7{,}63\ cm^3$

b/ Weight of water = 30x1,00 = 30 g

c/ Density of slip $= \frac{20+30}{7{,}63+30} = 1{,}33\ gcm^{-3}$

2/ A flint suspension of density 1,54 gcm^{-3} is made from 80 g of dry flint and 55 cm^3 of water. What is the density of the flint?

Material	Weight /g/	Volume /cm^3/	Density /gcm^{-3}/
Dry flint	80	$\frac{80}{d}$	d
Water	55	55	1,0
Suspension	135	$\frac{80}{d}+55$	1,54

Let d be the density of dry flint /gcm^{-3}/

Volume of flint $= \frac{80}{d}\ cm^3$

weight of water = 55 g

According to /30/

$$\text{the density of suspension} = \frac{\text{Total weight of components}}{\text{Total volume of components}}$$

$$1{,}54 = \frac{135}{\frac{80}{d}+55}$$

$$50{,}3\ d = 123{,}2$$

$$d = \frac{123,2}{50,3} = 2,45 \text{ gcm}^{-3}$$

3/ Equal weights of water and a powder material of density 2,5 gcm^{-3} are made into a slip. What will be its density?

Let d is the density of slip /gcm^{-3}/

x is the weight of water

x is also the weight of dry material

According to the eq./30/

$$d = \frac{2x}{\frac{x}{2,5} + x} = \frac{2x}{1,4x} = 1,43 \text{ gcm}^{-3}$$

Dilution Problems

The density of a slip is reduced by the addition of water, and the corresponding change in density, may be treated as follows:

The density of water is 1 gcm^{-3} and the necessary dilution is

$$\frac{E - F}{F - 1} \text{ cm}^3 \qquad /31/$$

of water added to every cm^3 of slip at Egcm^{-3} to give a resultant slip at Fgcm^{-3}.

Example

How much water must be added to 480 cm^3 of slip /density 1,8 gcm^{-3}/ to reduce its density to 1,65 gcm^{-3}; /$E = 1,8 \text{ gcm}^{-3}$ $F = 1,65 \text{ gcm}^{-3}$/

According to /31/

$$\frac{1,8-1,65}{1,65-1} = \frac{0,15}{0,65}$$ cm^3 of water for each cm^3 of "original" slip.

Hence total water required:

$$\frac{0,15}{0,65} \cdot 480 = 111 \text{ cm}^3$$

Brogniart's Formula

Calculations involving the liquid and solid components of a slip are often simplified by using Brogniart's Formula which may be applied to any volume of slip and any system of units. In general it becomes:

$$\text{Weight of dry material} = /\text{Weight of slip} - \text{Weight of water}/ \times \frac{d}{d-1} \quad \ldots\ldots\ldots \quad /32/$$

where d = density of the solid component.

In the above formula /32/ the "Weight of slip" and "Weight of water" must have the same volume.

Example

300 cm^3 of slip weigh 462 g

300 cm^3 of water weigh 300 g

Hence, according the formula /32/

$$\text{Dry content} = (462-300)\ \frac{2{,}5}{2{,}5-1} = 270 \text{ g}$$

The above principle is often used in particle size measurement /e.g. the hydrometer method/ for calculating the dry content of a sample in slip form. It is convenient to use a specific gravity bottle as the containing vessel. The bottle is half-filled with the slip to be tested, then the water is added to fill the bottle completely - it is then weighed. The weight of the bottle completely filled with water is obtained, and, since the weight of the bottle is the same in both cases, it follows that:

$$\text{weight of particles in sample} = \left[(\text{Wt. bottle+slip}) - (\text{Wt. bottle+water})\right] \times \frac{d}{d-1}$$

where d is the density of the dry material.

Example

In a hydrometer test on a sample of wet-ground alumina,

Weight of bottle + slip = 124,6 g

and Weight of bottle + water = 95,8 g

What weight of dry alumina /density = 3,64 gcm^{-3}/ was used in the test ?

Weight of dry alumina = $\left(124{,}6-95{,}8\right)\dfrac{3{,}64}{2{,}64} = 39{,}71$ g

Problems

1/ 200 cm^3 of slip weigh 298 g. What is its density ?

According eq. /15/

$$d_s = \frac{298}{200} = 1{,}49\ gcm^{-3}$$

2/ What volume of water /cm^3/ must be added to 40 g of dry glaze /density 2,9 gcm^{-3}/ to yield a slip at 1,5 gcm^{-3}

According eq/30/ Density of slip = $\dfrac{\text{Total weight of components}}{\text{Total volume of components}}$

$$1{,}5 = \frac{40+x}{\frac{40}{2{,}9}+x}$$

$$1{,}5\left(13{,}8+x\right) = 40 + x$$

$$0{,}5\ x = 40-20{,}7$$

$$x = \underline{38{,}6\ cm^3}$$

3/ A litre of slip weighs 1 578 g. The solid component has a density of 2,6 gcm^{-3}. Calculate the dry content of the slip.

According to Brogniart's Formula /32/

$$W_d = \left(W_s - W_w\right)\cdot \frac{d}{d-1}$$

$$W_d = \left(1578 - 1000\right)\cdot \frac{2{,}6}{2{,}6-1} = 578\ \frac{2{,}6}{1{,}6} = \underline{939\ g}$$

Dry content of the slip weighs 939 g.

4/ A vessel weighs 92,6 g when filled with slip, and 67,4 g when filled with water. What is the weight of solid particles in the slip ? /Density of the dry material is 3,26 gcm^{-3}/.

Again according to /32/

$$W_d = \left(W_s - W_v\right) \frac{d}{d-1} = \left(92,6 - 67,4\right) \frac{3,26}{3,26-1} = \underline{36,4\ g}$$

V. Body Calculations

Body Mixing

In the manufacture of all ceramic products the requisite quantities of components /flint, stone, ball clay, china clay, bone, etc./ are measured in terms of weight or volume then subjected to a mixing process.

For most ceramic bodies, the actual mixing takes place in/ slip form, which ensures an intimate blending of the constituents and hence a uniform product. The original quantity of each component may, however, be measured out in the dry state or in slip form.

"Dry" Measurement

The component powder materials are simply weighed out then transferred to the mixing ark-due allowance being made for any moisture content /see Chapter I/.

An older technique, sometimes used in the manufacture of bone china, is to fill and level-off a "standard box" with the dry powder component. A specified number of boxes of each material is then used in the body mix. This of course, is an attempt to measure the dry materials on a volume basis. It suffers from errors due to inconsistent packing, and variable moisture contents of the raw materials.

"Wet" Measurement

A widely used method, in practice, is to obtain a stock of each constituent material in slip form. If the consistency /density/ of each slip is known, then a given volume may be pumped into the mixing ark-and it is a simple matter to calculate the dry material involved.

Example

A mixing consists of 550 l of fireclay slip /at 1,25 gcm^{-3}/ and 70 l of flint slip /at 1,5 gcm^{-3}/. What is the percentage dry recipe of the mix /assuming that both components have a density /dry/ of 2,5 gcm^{-3}/.

Using Brongniart's Formula /see eq./32//:

1 l of fireclay slip has a dry content

$$\text{of } W_D = \left(W_s - W_w\right) \cdot \frac{d}{d-1} = \left(1250-1000\right) \frac{2,5}{2,5-1} = 250 \text{x} \frac{2,5}{1,5} = 417 \text{ g}$$

1 l of flint slip has a dry content

$$\text{of } W_D = \left(W_s - W_w\right) \frac{d}{d-1} = \left(1500-1000\right) \cdot \frac{2,5}{2,5-1} = 500 \text{x} \frac{2,5}{1,5} = 833,3 \text{ g}$$

Total amount of dry fireclay

$$= 550 \text{ x } 0,417 = 229,3 \text{ kg}$$

Total amount of dry flint

$$= 70 \text{ x } 0,833 = 58,3 \text{ kg}$$

Total amount of dry materials = 287,6 kg and the dry recipe is 80 % fireclay; 20 % flint.

The volume of each component slip may be measured in any convenient units: litres, cubic meters /m^3/ cubic decimetres /dm^3/ etc. Then the recipe may be written as e.g.:

14 l	ball clay	at 1,2 gcm^{-3} density /wet/
8,5 l	china clay	at 1,3 gcm^{-3} density
5 l	flint	at 1,5 gcm^{-3} density

2,5 l stone at 1,6 gcm^{-3} density

and it now becomes a simple matter to convert this into the corresponding "dry" recipe. Assuming that the density of each of the component of dry materials is 2,5 gcm^{-3}, then the "dry" recipe becomes

$$14\left(1{,}2 - 1\right)\frac{2{,}5}{2{,}5-1} = 4{,}67$$

$$8{,}5\left(1{,}3 - 1\right)\frac{5}{3} = 4{,}25$$

$$5\left(1{,}5 - 1\right)\frac{5}{3} = 4{,}17$$

$$2{,}25\left(1{,}6 - 1\right)\frac{5}{3} = 2{,}25$$

and the percentage recipe is:

Ball clay	30,4 %
China clay	27,7 %
Flint	27,2 %
Stone	14,7 %
	100,0 %

A further simplification is possible if the density of all the dry component is the same. In the above example, the density of each dry component was 2,50, and the factor $\frac{5}{3}$ appeared in the expression of each dry content. This constant factor $/\frac{5}{3}/$ may be omitted, since it does not affect the ratios between the weights of the component materials.

E.g.

Ball clay	$14 \times (1{,}2 - 1)$	=	2,8
China clay	$8{,}5 \times (1{,}3 - 1)$	=	2,55
Flint	$5 \times (1{,}5 - 1)$	=	2,5
Stone	$2{,}25 \times (1{,}6 - 1)$	=	1,35
			9,20

This is virtually the same dry recipe, which is clearly seen when it is converted to percentage form, giving:

Ball clay	30,4 %
China clay	27,7 %
Flint	27,2 %
Stone	14,7 %
	100,0 %

In general, then, if the density of each component is the same, to convert from a "wet" recipe to a "dry" recipe, apply the formula

$$V \times \left(d_w - 1 \right) \qquad /33/$$

to each component, where

V = the Volume and

d_w = the density of each wet component

/1 being the density of water/

<u>Example</u>

Calculate the percentage dry recipe of the following mix:

10,5 l ball clay at $d_w = 1{,}2\ \mathrm{gcm}^{-3}$

6,5 l china clay at $d_w = 1{,}3\ \mathrm{gcm}^{-3}$

4 l flint at $d_w = 1{,}6\ \mathrm{gcm}^{-3}$

2,5 l stone at $d_w = 1{,}6\ \mathrm{gcm}^{-3}$

Dry recipe		Percentage dry recipe is:
Ball clay	$10{,}5 \times (1{,}2-1) = 2{,}1$	26,4 %
China clay	$6{,}5 \times (1{,}3-1) = 1{,}95$	24.5 %
Flint	$4 \times (1{,}6-1) = 2{,}4$	30,2 %
Stone	$2{,}5 \times (1{,}6-1) = 1{,}5$	18,9 %
	7,95	100,0 %

Effect of Density

The assumption that all the components have a density of 2,50 is never strictly true. Materials, such as ball clay, china clay and stone, have a reasonably constant density and consequently cause very little variation in the final body from batch to batch.

Flint, however, has a variable density dependent upon the calcination process. Calcining is necessary to make the flints brittle and, therefore, easier to grind; but, during calcination, the density of the material could be reduced, theoretically, from approximately 2,65 to 2,30.

In a well-controlled calcination process, the fall in density is arrested at the value 2,50; on the other hand under-calcined flint has a higher density and over-calcined flint a lower density than 2,50.

Such variations may cause errors in the body mix if a "wet" recipe is used. To illustrate this, compare the dry contents of the following flint slips:

Slip A: 1 l at wet density $d_w = 1{,}6$ kgdm^{-3} ;
density of dry flint $d = 2{,}5$ kgdm^{-3}
Slip B: 1 l at wet density $d_w = 1{,}6$ kgdm^{-3} ;
density of dry flint $d = 2{,}4$ kgdm^{-3}

According to /32/

Dry content of Slip A .... $1{,}6-1 \cdot \frac{2{,}5}{1{,}5} = 1$ kg

Dry content of Slip B .... $1{,}6-1 \cdot \frac{2{,}4}{1{,}4} = 1{,}028$ kg

Both the volumes and the densities of the two slips are the same, and it becomes clear that a reduction in the density of the dry powder material causes an increase in the dry content of the slip.

A "wet" recipe determines the volume and density of the slip to be added to the mixing ark, but, even if these instructions are followed implicitly, errors in the body composition will occur if the density of the dry component changes.

Assuming a density of 2,50 for each the dry components, it has been shown that the dry recipe for the mix is:
/see p. 47 /

Ball clay	30,4 %
China clay	27,7 %
Flint	27,2 %
Stone	14,7 %

Suppose now that a batch mix was made using under-calcined flint /density = 2,60/. What effect would this have upon the dry recipe?

The calculation becomes:

Ball clay $= 14 \times (1,2 - 1)\frac{5}{3} = 4,67$

China clay $= 8,5 \times (1,3 - 1)\frac{5}{3} = 4,25$

Flint $= 5 \times (1,5 - 1)\frac{2,6}{1,6} = 4,06$

Stone $= 2,25 \times (1,6 - 1)\frac{5}{3} = 2,25$

$\overline{15,23}$ 100 %

and the percentage dry recipe is now:

Ball clay	30,6 %
China clay	27,9 %
Flint	26,7 %
Stone	14,8 %

i.e. the use of under-calcined flint has led to a reduction of 0,5% in the free silica content of the body.

The general ceramic implications of this effect may be summarized as follows:

Under-calcination of flint → Less SiO_2 in body → Tendency to craze the applied glaze

Over-calcination of flint → More SiO_2 in body → Tendency to peel the applied glaze

Density of the Body Slip

The component slius each have a density which ensures that its fluid properties are suitable for mixing. The final body slip usually has a density of about 1,35 gcm^{-3}-appropriate for further processing /lawning, magnetting, etc./

The density of the final body slip may be calculated from the "wet" recipe.

Example:

An earthenware body is made from:

18 l of ball clay slip at 1,2 kgdm^{-3}
11 l of china clay slip at 1,3 kgdm^{-3}
7,5 l of flint slip at 1,5 kgdm^{-3}
4,5 l of stone slip at 1,6 kgdm^{-3}

what is the density of the body slip ?

Then:

Volume of body slip = 18+11+7,5+4,5 = 41 l

and

Weight of body slip = 18x1,2 + 11x1,3 + 7,5x1,5 + 4,5x1,6 =
= 54,35 kg

Hence, Density of body slip = $\frac{54,35}{41}$ = 1,325 kgdm^{-3}

Problems

/Unless otherwise stated, assume that the density of all dry components is 2,5 gcm^{-3}/.

1/ Calculate the percentage dry recipe of the following mix: 500 l of fireclay slip at 1,2 gcm^{-3} and 60 l of flint slip at 1,6 gcm^{-3} /1,6 kgdm^{-3}/.

According to /32/

Dry content of fireclay in 1 l of slip $(1,2-1) \cdot \frac{5}{3} = 0,333$ kg/1 l

Dry content of flint in 1 l of slip $(1,6-1) \cdot \frac{5}{3} = 1$ kg/1 l

Dry fireclay	500 x 0,333	= 166,5 kg	73,5 %
Dry flint	60 x 1	= 60,- kg	26,5 %
		226,5 kg	100 %

2/ A mixing has the recipe:

60 l	ball clay	at 1,2 $\mathrm{kg/dm}^{-3}$
50 l	china clay	at 1,3 $\mathrm{kg/dm}^{3}$
25 l	flint	at 1,55 $\mathrm{kg/dm}^{3}$
12,5 l	stone	at 1,6 $\mathrm{kg/dm}^{3}$

What is the percentage dry recipe?

Dry content of

			kg	%
ball clay	$60 \times (1,2-1)\,\frac{5}{3}$	=	20	24,9
china clay	$50 \times (1,3-1)\,\frac{5}{3}$	=	25	31,1
flint	$25 \times (1,55-1)\,\frac{5}{3}$	=	22,9	28,5
stone	$12,5 \times (1,6-1)\,\frac{5}{3}$	=	12,5	15,5
			80,4	100,-

3/ A recipe calls for 12 l of flint slip at 1,6 gcm^{-3} /density of dry material 2,5 gcm^{-3}/. If a stock of flint slip is to be used at 1,55 gcm^{-3} /the dried material having a density of 2,45/, how many wet litres should be added ?

The 12 l of normal flint has a dry content of

$$12 \times (1,6 - 1)\frac{5}{3} = 12 \text{ kg}$$

The incorrect slip must have an equal dry content i.e.

$$x \cdot (1{,}55-1) \cdot \frac{2{,}45}{1{,}45} = 12 \; ; \quad x = \frac{12 \cdot 1{,}45}{2{,}45 \cdot 0{,}55} = 12{,}9 \text{ l of flint}$$

from stock

4/ The recipe of an earthenware body is:

17,5 l ball clay at 1,2 kg/dm^3 density

14,- l china clay at 1,3 kg/dm^3 density

6,5 l flint at 1,6 kg/dm^3

4,- l stone at 1,525 kg/dm^3

Calculate the percentage dry recipe and the density of the body slip.

		kg	%
Dry content of ball clay slip	$17{,}5 \cdot (1{,}2-1) \cdot \frac{5}{3} =$	5,83	25,5 %
Dry content of china clay slip	$14{,}- \cdot (1{,}3-1) \cdot \frac{5}{3} =$	7,-	30,7 %
Dry content of flint slip	$6{,}5 \cdot (1{,}6-1) \cdot \frac{5}{3} =$	6,5	28,5 %
Dry content of stone slip	$4 \cdot (1{,}525-1) \cdot \frac{5}{3} =$	3,5	15,3 %
	Σ	22,83 kg	100,- %

Volume of body slip:

17,5 + 14 + 6,5 + 4 = 42 l

Weight of body slip

$17{,}5 \cdot 1{,}2 + 14 \cdot 1{,}3 + 6{,}5 \cdot 1{,}6 + 4 \cdot 1{,}525 = 21 + 18{,}2 + 10{,}4 + 6{,}1 = 55{,}7$ kg

Density of body slip

$$\frac{55{,}7}{42} = 1{,}326 \text{ kg/dm}^3$$

5/ The recipe of a body is

75 l	ball clay	at	1,2 kg/dm^3
50 l	china clay	at	1,3 kg/dm^3
35 l	flint	at	1,6 kg/dm^3
15 l	stone	at	1,6 kg/dm^3

Analytical data of the components is:

	% SiO_2	% Loss-on-ignition
Ball clay	50,5	10,2
China clay	49,5	11,8
Flint	97,0	0,5
Stone	72,6	1,5

What increase in flint /"wet[1]"/ is required to give a 1 % increase in the percentage silica /calculated on the fired body/?

Material	Dry recipe	Fired weight	Weight of SiO_2 in fired material
Ball clay	$75.0,2.\frac{5}{3} = 25$ kg	$\frac{25}{100} \times 89,8 = 22,45$ kg	$50,5 \times \frac{25}{100} =$ $= 12,625$ kg
China clay	$50.0,3.\frac{5}{3} = 25$ kg	$\frac{25}{100} \times 88,2 = 22,05$ kg	$49,5 \times \frac{25}{100} =$ $= 12,375$ kg
Flint	$35.0,6.\frac{5}{3} = 35$ kg	$\frac{35}{100} \times 99,5 = 34,825$ kg	$97 \times \frac{35}{100} =$ $= 33,95$ kg
Stone	$15.0,6.\frac{5}{3} = 15$ kg	$\frac{15}{100} \times 98,5 = 14,775$ kg	$72,6 \times \frac{15}{100} =$ $= 10,89$ kg
Totals		94,1 kg	69,84 kg

Percentage silica /calculated on fired body/

$$= \frac{69,84}{94,1} \times 100 = 74,22\ \%$$

Let x[1] be the amount of flint slip required to give 75,22 % silica /calculated on the fired body/. Then :

Material	Dry recipe	Fired weight	Weight of SiO_2 in fired material
Ball clay	$75.0,2.\frac{5}{3} = 25$ kg	$\frac{25}{100}.89,8=22,45$ kg	$50,5.\frac{25}{100} =$ $= 12,625$ kg
China clay	$50.0,3.\frac{5}{3} = 25$ kg	$\frac{25}{100}.88,2=22,05$ kg	$49,5.\frac{25}{100} =$ $= 12,375$ kg
Flint	$x.0,6.\frac{5}{3} = x$	$\frac{x}{100}.99,5=0,995\ x$	$97\ \frac{x}{100} = 0,97x$
Stone	$15.0,6.\frac{5}{3} = 15$ kg	$\frac{15}{100}.98,5=14,775$ kg	$72,6.\frac{15}{100} =$ $= 10,89$ kg
Totals		$59,275+0,995x$	$35,89+0,97x$

and $\frac{35,89 + 0,97\ x}{59,275+0,995\ x} \ .\ 100 = 75,22$

$$(35,89 + 0,97\ x)\ .\ 100 = 75,22\,(59,275 + 0,995\ x)$$

Solving this equation gives $x = 39,25$ l /or dm^3/ i.e. there must be an increase of

$$39,25 - 35 = 4,25 \text{ l of flint slip.}$$

VI. Introduction to Glaze Calculations

Chemical equations are often used in ceramic calculations. All chemical calculations are based on the use of formulae and equations in conjuction with atomic weights.

It is important to understand the use of these fundamental calculations as applied to ceramic materials.

To calculate the molecular weight of soda ash,Na_2CO_3. Using the atomic weights of each atom, /see Table II., p.85/

two atoms of sodium = 2 x 23 = 46

one atom of carbon = 1 x 12 = 12

three atoms of oxygen = 3 x 16 48

106

The molecular weight = 106

To calculate the molecular weight of white lead,

$Pb(OH)_2 \cdot 2PbCO_3$,

3 atoms of Pb = 3 x 207 = 621
8 atoms of O = 8 x 16 = 128
2 atoms of H = 2 x 1 = 2
2 atoms of C = 2 x 12 = 24
775

The molecular weight of white lead = 775

Use of Chemical Equations

Chemical equations describe not only the nature of the atoms and molecules of substances taking part in a chemical change, but also the quantitative relationship between them. For example, consider the equation

$$CaCO_3 = CaO + CO_2$$

The weight of one molecule of calcium carbonate expressed in grams = 40+12+(3x16) = 100. The gram-molecular weight of CaO = 56 and the gram-molecular weight of CO_2 = 44.

This means that 100 g of calcium carbonate on heating will yield 56 g of lime and 44 g of carbon dioxide.

The equation also indicates the volume of gas liberated. This is based on the fact that the molecular weight of any gas, expressed in grams occupies 22,4 litres at N.T.P. /Normal Temperature and Pressure/, i.e. $0^{\circ}C$ and 10^5 Pa pressure /reference Avogadro's Hypothesis/. In the above equation 100 g of calcium carbonate on heating would liberate 22,4 litres of carbon dioxide at N.T.P.

These principles are used in the following examples:

If one ton of china clay is calcined to 1,100°C, what is the loss in weight in kg ?

The equation for this reaction may be written /Table III.,p.86/

$Al_2O_3.2SiO_2.2H_2O = Al_2O_3 + 2SiO_2 + 2H_2O$

The loss in weight is due to the vaporization of the chemically combined water.

258 parts by weight of china clay suffers a loss in weight of 36 parts by weight of chemically combined water;

258 tons of china clay loses 36 tons of water;

1 ton of china clay loses $\frac{36}{258}$ tons of water;

or 1 kg of china clay loses $\frac{36}{258} = 0{,}1395$ kg of water

A frit mixture contains 100 kg of calcium carbonate. Calculate the volume of carbon dioxide /m^3/ which will be liberated on fritting at a temperature of 1,000°C.

$$44 \text{ g } CO_2 \equiv 22{,}4 \text{ litres at N.T.P.}$$

100 g of $CaCO_3$ will yield 44 g of CO_2 i.e. 22,4 l at N.T.P.

100 kg .. 10^5g of $CaCO_3$ will yield 44.10^3g of CO_2

i.e. $22{,}4.10^3$l at N.T.P.

100 kg of $CaCO_3$ will yield 22,4 m^3 of CO_2 at N.T.P.

Applying Charles' law :

$$22{,}4\ \frac{1000 + 273}{273} = 104{,}5 \text{ m}^3\ CO_2 \text{ at } 1000^\circ C$$

Oxides

The molecular formulae of glazes and frits are given in terms of molecular parts of the constituent oxides. The oxides are classified into three main group:

/1/ Acidic Oxides

They are the oxides of non-metals. If soluble in water, they combine with it, forming an acid. They combine with bases to form salts. Silica SiO_2 and boric oxide B_2O_3 are the two main acidic oxides used in frits and glazes. They combine with other elements to form silicate and borate glasses.

/2/ Basic Oxides

They may be considered at the oxides of metals. They react with acids to form a salt and water only. If soluble in water they yield hydroxides.

The main basic oxides used in the ceramic industry are listed below:

K_2O CaO BaO PbO Na_2O MgO ZnO

/3/ Amphoteric Oxides

An amphoteric oxide may exhibit either basic or acidic properties. Alumina, Al_2O_3 reacts with dilute hydrochloric acid to yield aluminium chloride and water, and thus behaves as a basic oxide;

$$Al_2O_3 + 6\ HCl = 2\ AlCl_3 + 3\ H_2O$$

but with sodium hydroxide, alumina reacts as an acidic oxide and forms sodium aluminate:

$$Al_2O_3 + 2\ NaOH = 2\ NaAlO_2 + H_2O$$

Alumina is the main amphoteric oxide in frits and glazes.

Relationship between Percentage Composition and Formula

The chemical analysis of a pure compound determines the nature and quantity of each constituent chemical substance. The result of a quantitative analysis is given in terms of percentage composition, or proportion by weight of each element present, e.g. a compound containing carbon, hydrogen, nitrogen and sulphur on analysis is found to have the following percentage composition:

C = 41,4 %
H = 5,8 %
N = 16,1 %
S = 36,7 %

If the figures for the percentage composition are divided by the atomic weight of the elements concerned, then the result of this calculation gives the simplest possible formula to the compound. The "empirical" or "simplest possible" formula only indicates the proportions of the atoms in the molecules, but does not give their actual number. It is necessary to appreciate that the percentage composition when divided by the appropriate atomic weight gives the "simplest possible" formula and that this is adequate for most ceramic materials, since the correct ratio between the constituent elements is maintained.

This is true not only with pure chemical compounds, but the same considerations apply to ceramic materials, although the formulae of some of them are expressed in terms of oxides, e.g. potash felspar, $K_2O.Al_2O_3.6SiO_2$.

The percentage composition of china clay is given as:

SiO_2 = 46,51
Al_2O_3 = 39,53
H_2O = 13,96

Calculate its molecular formula.

$$SiO_2\ 46.51 : 60 = 0,775$$
$$Al_2O_3\ 39,53 : 102 = 0,387$$
$$H_2O\ 13,96 : 18 = 0,775$$

Dividing throughout by the smallest number /0,387/ the empirical formula = $Al_2O_3.2SiO_2.2H_2O$.

The molecular formula for china clay = $Al_2C_3.2SiO_2.2H_2O$

In the above example the percentage composition is given in terms of oxides, molecular weights of which must be used in place of atomic weights. Similar principles apply in calculating the molecular formula of a glaze from its percentage composition.

A simple glaze has the following percentage composition:

PbO	63,90
Al_2O_3	5,87
SiO_2	30,23

Dividing the percentage composition of each oxide by its molecular weight the ratios become:

$$\frac{63,90}{223}\,PbO : \frac{5,87}{102}\,Al_2O_3 : \frac{30.23}{60}\,SiO_2$$
$$= 0,287\ PbO : 0,058\ Al_2O_3 : 0,504\ SiO_2$$

In calculating the empirical formula, each molecular part would have been divided by the smallest number /in this case 0,058/. However, in ceramics a convention is adopted with glazes, that the sum of the basic oxides be equal to unity. This puts all glaze formulae on a basis which enables the many different types of glazes to be compared, one with another. A knowledge of glaze formulae used in this form is of paramount importance to the glaze technologist. He can forecast such physical properties as fusibility, solubility, etc., from such information.

In the above calculation, the basic oxide is PbO and dividing throughout by 0,287 the glaze formula becomes:

$$1\ PbO;\ 0{,}202\ Al_2O_3;\ 1{,}756\ SiO_2$$

The oxides are usually written in the order shown, i.e. basic, amphoteric and acidic.

Later, the "molecular weight" of glazes is referred to. It should be noted that this weight is not the "true molecular weight", but is really a "formula weight". It is an arbitrary figure calculated from the formula obtained by using the above convention. The "molecular weight" figure as used in glaze calculations has no true significance, since it has been computed from this artificially devised formula.

Given the Formula. Calculate the Percentage Composition

The reverse procedure to that used in the previous problem is shown below:

Given the formula of sodium carbonate, Na_2CO_3, calculate the percentage composition in terms of
/a/ the elements Na,C and O: and /b/ the oxides Na_2O and CO_2.

The molecular weight of Na_2CO_3 = 106.

/a/ Sodium $\frac{46}{106} \times 100 = 43{,}4\ \%$

Carbon $\frac{12}{106} \times 100 = 11{,}3\ \%$

Oxygen $\frac{48}{106} \times 100 = 45{,}3\ \%$

/b/ $Na_2O\ (2 \times 23) + 16 = 62$

$\frac{62}{106} \times 100 = 58{,}5\ \%$

$$CO_2 \quad 12 + (2 \times 16) = 44$$

$$\frac{44}{106} \times 100 = 41{,}5\ \%$$

Further example

Given the formula of a glaze as:

$$\left.\begin{matrix} 0{,}6\ PbO \\ 0{,}4\ Na_2O \end{matrix}\right\} \ 0{,}25\ Al_2O_3 \ \left\{\begin{matrix} 1{,}9\ SiO_2 \\ 0{,}4\ B_2O_3 \end{matrix}\right.$$

Calculate the percentage composition.

PbO	0,6 x 223 =	133,8
Na_2O	0,4 x 62 =	24,8
Al_2O_3	0,25x 102 =	25,5
SiO_2	1,9 x 60 =	114,0
B_2O_3	0,4 x 70 =	28,0
		326,1

326,1 represents the "molecular weight" of the glaze.

As stated previously it is not a "true molecular weight," but, in fact, a "formula weight".

By multiplying throughout by $\frac{100}{326{,}1}$ the percentage composition is:

PbO	41,04
Na_2O	7,59
Al_2O_3	7,82
SiO_2	34,96
B_2O_3	8,59

It can be seen in the above calculation that

<u>Molecular Weight x Molecular Parts = Parts by Weight</u> /34/

Using sodium oxide as an example:

Na_2O molecular weight = 62
molecular parts = 0,4
and their product = 24,8

This relationship is used throughout glaze calculations.

Recipe of a Glaze

It has been shown that the chemical analysis of a glaze /i.e. the weights of the constituent oxides present/ can be written in terms of a molecular formula. Also, that given the molecular formula of a glaze the percentage composition /or analysis/ may be computed.Could these weights of the various oxides actually be used to manufacture the glaze ?

On a small scale in the laboratory, it may be possible to obtain and weigh out the PbO, Al_2O_3, etc., and to make the glaze. The percentage composition would then become the actual working recipe of the glaze.

For industrial-scale production however, it is both uneconomical and impractical to manufacture glazes from raw oxides. Other materials are, therefore, used to introduce these oxides.

The choice of raw materials depends upon many factors, such as:

/1/ Availability of the material in a pure state. The compound need not be 100 % pure, but it should be available in a form which does not have variable amounts of impurities from batch to batch.

/2/ Cost of raw material.

/3/ Suitability of the material for continuous use under factory conditions. For example, certain lead compounds may prove to be poisonous and to have a cumulative effect when used by operatives over long periods of time.

Given a Glaze Formula, Calculate a Recipe /see Table IV. p.87/

A simple glaze has the following formula:

$$PbO;\ 0{,}2\ Al_2O_3;\ 2{,}9\ SiO_2$$

Lead oxide PbO . The following compounds contain PbO which could, theoretically, be used to introduce this oxide into the glaze:

Litharge	PbO
Red lead	Pb_3O_4
White lead	$Pb(OH)_2 .\ 2\ PbCO_3$
Lead bisilicate	$PbO.2\ SiO_2$

Litharge and red lead do not suspend well, are costly and present the risk of lead poisoning.

White lead was, in the past, used as a source of PbO because of its suspending properties and availability. However, its use has been prohibited. White lead is a potential source of lead poisoning, because it is soluble in the hydrochloric acid contained in the gastric juices.

Lead frits are generally used today to introduce the PbO content. Lead bisilicate is a common form of lead frit extensively used because it is virtually insoluble in dilute hydrochloric acid.

Alumina /Al_2O_3/. Two commercially available compounds containing Al_2O_3 are:

Bauxite	$Al_2O_3 .\ 2\ H_2O$
China clay	$Al_2O_3 .\ 2SiO_2 .2\ H_2O$

China clay is preferred because it is a comparatively cheap product. Its flaky structure also helps in the suspension of the glaze.

Silica /SiO_2/. Flint is usually the main form of SiO_2, but quartz sand of high purity is sometimes used.

The three raw materials which may be used to compound this glaze would then be:

Lead bisilicate
China clay

Flint

The calculation of the recipe for this glaze is shown in the table below:

Material	Molecular weight	Molecular parts	Parts by weight	PbO	Al_2O_3	SiO_2
Lead bisilicate	343	1,0	343	1,0		2,0
China clay	258	0,2	51,6		0,2	0,4
Flint	60	0,5	30,0			0,5
				1,0	0,2	2,9

The "parts by weight" column gives the final recipe:

Lead bisilicate	343,0
China clay	51,6
Flint	30,0

Glaze calculations are best written out in the table form as shown above.

All data to the left of the double vertical line refer to the material as a whole. Data to the right refer to the oxide components involved.

Note. 0,2 molecular part of china clay brings in 0,2 molecular part of Al_2O_3 and 0,4 molecular part of SiO_2.

The general rule:

Molecular Weight x Molecular Part = Parts by Weight /34/

is used and these values are set out as shown in the second, third and fourth columns of the table.

In the past white lead may have been used in the calculation instead of lead bisilicate, then the result would have been:

Material	Molecular weight	Molecular parts	Parts by weight	PbO	Al_2O_3	SiO_2
White lead	775	0,333	258	1,0		
China clay	258	0,200	52		0,2	0,4
Flint	60	2,500	150			2,5
				1,0	0,2	2,9

In the molecular parts column, 0,333 molecule of white lead is required to produce one molecule of PbO in the finished glaze for the following reason:

One molecule of white lead produces three molecules of lead oxide on calcination.

$$Pb(OH)_2 \cdot 2PbCO_3 = 3PbO + 2CO_2 + H_2O$$

CO_2 and H_2O are non-permanent oxides and do not form compounds with other glaze constituents.

Many compounds used in frits and glazes behave in a similar manner. A list of compounds is given in Table IV p.87. The table gives the formula, molecular weight and permanent oxides obtained on heating these compounds.

A further example of calculating the recipe of a glaze is given below. The principle is exactly the same as in the previous example but, in many glaze calculations, more arithmetic is involved. This is due in some cases to such felspathic rocks as stone which are not pure chemical compounds. There are many different varieties of stone, each having its own composition and formula.

The formula of a glaze is:

$$\left.\begin{array}{l} 0{,}081\ K_2O \\ 0{,}028\ Na_2O \\ 0{,}293\ CaO \\ 0{,}598\ PbO \end{array}\right\}\ 0{,}232\ Al_2O_3;\ 4{,}065\ SiO_2$$

Calculate a recipe using the following raw materials:

Whiting, lead bisilicate, china clay, flint, and stone; the stone has a molecular formula:

$$\left.\begin{array}{l} 0{,}412\ K_2O \\ 0{,}143\ Na_2O \\ 0{,}180\ CaO \end{array}\right\}\ 1{,}0\ Al_2O_3;\ 7{,}1\ SiO_2$$

Writing out the calculation in the usual table form /see p.67/.

Material	Molecular weight	Molecular parts	Parts by weight	PbO	K_2O	Na_2O	CaO	Al_2O_3	SiO_2
Lead bisilicate	343	0,598	205,1	0,598					1,196
+ Stone	585,7	0,197	115,4		0,081	0,028	0,035	0,197	1,399
Whiting	100	0,258	25,8				0,258		
China clay	258	0,035	9,0					0,035	0,070
Flint	60	1,400	84,0						1,400
				0,598	0,081	0,028	0,293	0,232	4,065

The recipe is

Lead bisilicate	205,1
Stone	115,4
Whiting	25,8
China clay	9,0
Flint	84,0

+In the above calculation the molecular weight of the stone was calculated in the same way as the molecular weight of any other compound, i.e., see p.68

$$\begin{array}{lrl} K_2O & 94 \times 0{,}412 & = 38{,}7 \\ Na_2O & 62 \times 0{,}143 & = 8{,}9 \\ CaO & 56 \times 0{,}180 & = 10{,}1 \\ Al_2O_3 & 102 \times 1{,}000 & = 102{,}0 \\ SiO_2 & 60 \times 7{,}100 & = 426{,}0 \\ \hline & & 585{,}7 \end{array}$$

The stone is used as a raw material essentially to introduce the alkali content.

Considering K_2O,

0,412 molecular part K_2O $\equiv$ 1 molecule of stone

1 molecular part K_2O $\equiv$ $\frac{1}{0{,}412}$ molecule of stone

0,081 molecular part K_2O $\equiv$ $\frac{1}{0{,}412} \times 0{,}081$ molecule of stone

$=$ 0,197 molecular parts of stone

The calculation shows that 0,197 molecular part of stone is required to introduce the requisite molecular part of K_2O, namely 0,081. If 0,197 molecular part of stone is used, then at the same time, the following amounts of other oxides are introduced.

Na_2O $0{,}143 \times 0{,}197 = 0{,}028$

CaO $0{,}180 \times 0{,}197 = 0{,}035$

Al_2O_3 $1{,}000 \times 0{,}197 = 0{,}197$

SiO_2 $7{,}100 \times 0{,}197 = 1{,}399$

The K_2O and Na_2O are now equivalent to the molecular parts as required by the glaze formula. Since stone is a flux and the alkalis are the active part of the flux, then the stone is introduced to satisfy the K_2O and Na_2O requirements. 0,197 molecular part of stone, in this case meets the requirements of K_2O and Na_2O. This is so because the question has been formulated in such a way that the alkali oxides are in the correct ratio to each other. If this was not the case, some other material would have to be introduced to make up for the deficiency of one of the oxides.

Given the Recipe of a Glaze. Calculate the Formula

A simple example is given which is the reverse procedure of the previous one.

Calculate the formula of a glaze which has the following recipe:

Lead bisilicate	50
China clay	28
Flint	10

Using the glaze calculation table:

Material	Molecular weight	Molecular parts	Parts by weight	PbO	Al_2O_3	SiO_2
Lead bisilicate	343	0,146	50	0,146		0,292
China clay	258	0,108	28		0,108	0,216
Flint	60	0,167	10			0,167
				0,146	0,108	0,675

Bringing the basic oxides to unity, divide throughout by 0,146. Glaze formula PbO; 0,740 Al_2O_3; 4,623 SiO_2.

0,146 molecular part for lead bisilicate is calculated by dividing the parts by weight /obtained from the recipe/ by the molecular weight: $\frac{50}{343}$ = 0,146. The molecular parts for china clay and flint are calculated in a similar manner.

Further example

Calculate the formula of a glaze which has the following recipe:

Lead bisilicate	171,5
Whiting	23,0
Stone	120,4
China clay	32,2
Flint	30,0

The formula of the stone is:

$$\left.\begin{array}{ll}0{,}28 & CaO\\ 0{,}62 & K_2O\\ 0{,}10 & Na_2O\end{array}\right\} Al_2O_3.7SiO_2$$

Material	Molecular weight	Molecular parts	Parts by weight	PbO	CaO	K_2O	Na_2O	Al_2O_3	SiO_2
Lead bisilicate	343	0,500	171,5	0,500					1,000
Whiting	100	0,230	23,0		0,230				
Stone	602,2	0,200	120,4		0,056	0,124	0,020	0,200	1,400
China clay	258	0,125	32,2					0,125	0,250
Flint	60	0,500	30,0						0,500
				0,500	0,286	0,124	0,020	0,325	3,150

To calculate the molecular weight of the stone:

CaO 56 x 0,28 = 15,68

K_2O 94 x 0,62 = 58,28

Na_2O 62 x 0,10 = 6,20

Al_2O_3 102 x 1,0 = 102,00

SiO_2 60 x 7,0 = 420,00

602,16

Dividing throughout by 0,930 to bring basic oxides to unity, the glaze formula is:

$$\left.\begin{array}{ll} 0{,}538 & PbO \\ 0{,}307 & CaO \\ 0{,}133 & K_2O \\ 0{,}022 & Na_2O \end{array}\right\} 0{,}349\ Al_2O_3 \left\{ 3{,}387\ SiO_2 \right.$$

Problems

/1/ Calculate the empirical formula from the percentage composition of the following compounds:

/a/ Fe = 72,4 /b/ Fe = 77,78 /c/ K = 38,61
O = 27,6 O = 22,22 N = 13,86
O = 47,53

a/ Atomic weight of Fe = 55,85 /see Table II p.85/
and of O = 16,00

The relative number of atoms in the compound is:

$$\frac{72{,}4}{55{,}85} : \frac{27{,}6}{16} = 1{,}296 : 1{,}725 \doteq 3 : 4$$

The empirical formula of the compounds is Fe_3O_4.

b/ $$\frac{77{,}78}{55{,}85} : \frac{22{,}22}{16} = 1{,}3926 : 1{,}388 \doteq 1 : 1$$

The compound is FeO

c/ Atomic weight of K = 39
N = 14

The relative number of atoms in the compounds is:

$$\frac{38{,}61}{39} : \frac{13{,}86}{14} : \frac{47{,}83}{16} = 0{,}99 : 0{,}99 : 2{,}99 \doteq 1:1:3$$

The compound is KNO_3

/2/ Calculate the percentage composition of the following compounds, in terms of oxides /including water/:

/a/ Borax crystals	$Na_2B_4O_7.10H_2O$	/Table IV p.67/
/b/ Lead bisilicate	$PbO.2SiO_2$	
/c/ Felspar	$K_2O.Al_2O_3.6SiO_2$	
/d/ Silicic acid	H_2SiO_3	

a/ $Na_2B_4O_7.10H_2O \rightarrow Na_2O.2B_2O_3.10H_2O$

Atomic weights of oxides:

$Na_2O \rightarrow 2 \times 23 + 16 = 62$

$B_2O_3 \rightarrow 2 \times 11 + 3 \times 16 = 70$; $2\ B_2O_3 \rightarrow 140$

$10\ H_2O \rightarrow 10\ (2 + 16) = 180$

Atomic weight of the compound is 382

Percentage composition

$Na_2O : \frac{62}{382} . 100 \rightarrow 16,2\ \%$

$B_2O_3 : \frac{140}{382} . 100 \rightarrow 36,6\ \%$

$H_2O : \frac{180}{382} . 100 \rightarrow 47,1\ \%$

b/ $PbO.2SiO_2$

Atomic weights of oxides

$PbO \rightarrow 207 + 16 = 223$

$2SiO_2 \rightarrow 2(28+32) = 120$; compound atomic weight = 343

Percentage composition:

$PbO \rightarrow \frac{223}{343} . 100 = 65\ \%$

$2SiO_2 \rightarrow \frac{120}{343} . 100 = 35\ \%$

c/ Felspar $K_2O.Al_2O_3.6SiO_2$

According to Table IV p.87 the atomic weight of Felspar is 556

$$K_2O \rightarrow \frac{94}{556} \cdot 100 = 16,9 \%$$

$$Al_2O_3 \rightarrow \frac{102}{556} \cdot 100 = 18,3 \%$$

$$6SiO_2 \rightarrow \frac{360}{556} \cdot 100 = 64,7 \%$$

d/ Silicic acid H_2SiO_3 ; atomic weight is 78

$$SiO_2 \rightarrow \frac{60}{78} \cdot 100 = 76,9 \%$$

$$H_2O \rightarrow \frac{18}{78} \cdot 100 = 23,1 \%$$

/3/ If one ton of whiting is calcined to 1,000°C, what is the loss in weight.

According to Table IV on the p.87the atomic weight of whiting ($CaCO_3$) is 100

$$CaO \rightarrow \frac{40+16}{100} \cdot 100 = 56 \%$$

$$CO_2 \rightarrow \frac{12+2x16}{100} \cdot 100 = 44 \%$$

The loss is 44 % i.e. in weight 440 kg.

/4/ A glaze is analysed and found to have the following percentage composition:

SiO_2 = 66,96 CaO = 10,94

Al_2O_3 = 14,23 K_2O = 7,87

Calculate the molecular formula.

Atomic weights of oxides are as follows:

$SiO_2 \rightarrow 60$; $Al_2O_3 \rightarrow 102$; $CaO \rightarrow 56$; $K_2O \rightarrow 94$

$$\frac{66,96}{60}\,SiO_2 : \frac{14,23}{102}\,Al_2O_3 : \frac{10,94}{56}\,CaO : \frac{7,87}{94}\,K_2O =$$

$$= 1,116\ SiO_2 : 0,14\ Al_2O_3 : 0,195\ CaO : 0,084\ K_2O$$

Dividing throughout by the smallest number /0,084/ the empirical formula will be:

$$13,28\ SiO_2 : 1,666\ Al_2O_3 : 2,321\ CaO : 1\ K_2O$$

To bring the basic oxides to unity it is necessary to divide throughout by 3,321 /i.e. 2,321 CaO + 1 K_2O/.

Then the molecular formula will be :

$$\left.\begin{matrix} 0,7\ CaO \\ 0,3\ K_2O \end{matrix}\right\}\ 0,5\ Al_2O_3 \quad \left\{\ 4SiO_2\right.$$

/5/ The analysis of a glaze is given as follows:

PbO	53,24 %
CaO	5,72 %
Al_2O_3	5,21 %
SiO_2	35,81 %

Calculate the molecular formula.

$$\frac{53,24}{223}\,PbO : \frac{5,72}{56}\,CaO : \frac{5,21}{102}\,Al_2O_3 : \frac{35,81}{60}\,SiO_2 =$$

$$= 0,2387\ PbO : 0,1021\ CaO : 0,0511\ Al_2O_3 : 0,5968\ SiO_2$$

Dividing throughout by the smallest number /0,0511/ we obtain:

$$4,6712\ PbO : 1,998\ CaO : 1\ Al_2O_3 : 11,6791\ SiO_2$$

To bring the basic oxide to unity it is necessary to divide throughout by 6,6692 /i.e. 4,6712 PbO + 1,998 CaO/

$$\left.\begin{matrix} 0,7\ PbO \\ 0,3\ CaO \end{matrix}\right\}\ 0,15\ Al_2O_3 \quad \left\{\ 1,75\ SiO_2\right.$$

/6/ The percentage composition of a glaze is found by analysis to be:

PbO	22,80
Na_2O	6,96
K_2O	11,54
Al_2O_3	9,70
SiO_2	41,00
B_2O_3	8,00

Report these results as a glaze formula.

Atomic weights of oxides are as follows:

PbO → 223; Na_2O → 62; K_2O → 94; Al_2O_3 → 102; SiO_2 → 60; B_2O_3 → 70

$$\frac{22,8}{223}\ PbO : \frac{6,96}{62}\ Na_2O : \frac{11,54}{94}\ K_2O : \frac{9,7}{102}\ Al_2O_3 : \frac{41}{60}\ SiO_2 : \frac{8}{70}\ B_2O_3 =$$

$$= 0,1022\ PbO : 0,1122\ Na_2O : 0,1227\ K_2O : 0,095\ Al_2O_3 : 0,6833\ SiO_2 : 0,1142\ B_2O_3$$

Dividing throughout by the smallest number /0,095/ we obtain

$$1,076\ PbO: 1,181\ Na_2O: 1,291\ K_2O: 1\ Al_2O_3: 7,193\ SiO_2: 1,202\ B_2O_3$$

To bring the basic oxides to unity it is necessary to divide throughout by 3,548 /i.e. 1,076 PbO + 1,181 Na_2O + 1,291 K_2O/

The glaze formula will be then:

$$\left.\begin{array}{ll} 0,303 & PbO \\ 0,333 & Na_2O \\ 0,364 & K_2O \end{array}\right\}\ 0,282\ Al_2O_3 \qquad \left\{\begin{array}{ll} 2,027 & SiO_2 \\ 0,339 & B_2O_3 \end{array}\right.$$

/7/ A glaze on analysis is found to have the following percentage composition:

SiO_2	51,6
Al_2O_3	8,7
PbO	33,6
K_2O	6,1

Calculate:

/a/ the glaze formula; and

/b/ a recipe for the glaze

using china clay, lead bisilicate, potash felspar and flint.

Atomic weights of oxides are as follows:

SiO_2 - 60 ; Al_2O_3 - 102 ; PbO - 223 ; K_2O - 94

$$\frac{51,6}{60}\ SiO_2 : \frac{8,7}{102}\ Al_2O_3 : \frac{33,6}{223}\ PbO : \frac{6,1}{94}\ K_2O =$$

$$= 0,86\ SiO_2 : 0,0853\ Al_2O_3 : 0,1506\ PbO : 0,0649\ K_2O$$

Dividing throughout by 0,0649 we obtain:

$$13,25\ SiO_2 : 1,314\ Al_2O_3 : 2,32\ PbO : 1\ K_2O$$

Dividing by 3,32 /i.e. the sum of basic oxides 2,32 PbO+1 K_2O/ we obtain:

$$\left.\begin{matrix} 0,699\ PbO \\ 0,301\ K_2O \end{matrix}\right\} 0,395\ Al_2O_3 \quad \left\{ 3,99\ SiO_2 \right.$$

which is the glaze formula

According the Table IV on the page 87/ the material to be used posses following formulae and weights

China clay $Al_2O_3.2SiO_2.2H_2O(258) \rightarrow Al_2O_3(102) + 2SiO_2(2x60)$

Lead bisilicate $PbO.2SiO_2(343) \rightarrow PbO(223) + 2SiO_2\ (2x60)$

Potash felspar $K_2O.Al_2O_3.6SiO_2(556) \rightarrow K_2O(94) + Al_2O_3(102) + 6SiO_2(6x60)$

Flint $SiO_2(60)$

The recipe for the glaze will be as follows:

Lead bisilicate	239,7	parts
Felspar	167,4	-"-
China clay	24,2	-"-
Flint	35,88	-"-

as confirmed by following table:

Material	Molecular weight	Molecular parts	Parts by weight	PbO	K_2O	Al_2O_3	SiO_2
Lead bisilicate	343	0,699	239,7	0,699			1,398
Felspar	556	0,301	167,4		0,301	0,301	1,806
China clay	258	0,094	24,2			0,094	0,188
Flint	60	0,598	35,88				0,598
				0,699	0,301	0,395	3,990

/8/ Calculate the working recipe for a glaze of molecular formula:

$$\left.\begin{array}{ll} 0{,}6 & PbO \\ 0{,}3 & CaO \\ 0{,}1 & K_2O \end{array}\right\} 0{,}18\ Al_2O_3;\ 2{,}0\ SiO_2$$

using lead bisilicate and potash felspar for two of the materials.

We shall calculate as follows:

Material	Molecular weight	Molecular parts	Parts by weight	PbO	CaO	K_2O	Al_2O_3	SiO_2
Lead bisilicate	343	0,6	205,8	0,6				1,2
Whiting	100	0,3	30,0		0,3			
Felspar	556	0,1	55,6			0,1	0,1	0,6
China clay	258	0,08	20,6				0,08	0,16
Flint	60	0,04	2,4					0,04
			Σ	0,6	0,3	0,1	0,18	2,00

The working recipe for the glaze will be:

Lead bisilicate	205,8 parts
Whiting	30,- -"-

Felspar	55,6 parts
China clay	20,6 -"-
Flint	2,4 -"-

/9/ Calculate the recipe of a frit:

$$\left.\begin{array}{l} 0{,}72\ PbO \\ 0{,}28\ Na_2O \end{array}\right\} \begin{array}{l} 0{,}90\ SiO_2 \\ 0{,}56\ B_2O_3 \end{array}$$

using red lead, borax, and flint.

Molecular weights of materials to be used / see Table IV on the p.87 /

Read lead : $Pb_3O_4 (685) \rightarrow 3\ PbO\ (3x223)$

Borax: $Na_2B_4O_7 \cdot 10H_2O (382) \rightarrow Na_2O (62) + 2\ B_2O_3\ (2x70)$

Flint: $SiO_2 (60)$

Material	Molecular weight	Molecular parts	Parts by weight	PbO	Na_2O	B_2O_3	SiO_2
Read lead	685	0,72	493,2 3PbO 1PbO 164,4	0,72			
Borax	382	0,28	106,96		0,28	0,56	
Flint	60	0,9	54				0,9
			Σ	0,72	0,28	0,56	0,9

The working recipe for the glaze will be as follows:

Read lead	164,4	parts
Borax	107,0	-"-
Flint	54,0	-"-

/10/ What is the recipe of a lead frit PbO; 0,2 Al_2O_3; 2 SiO_2 using red lead, china clay, and flint ?

Material	Molecular weight	Molecular parts	Parts by weight	PbO	Al_2O_3	SiO_2
Read lead	685	1	$\frac{685}{3}=228,3$	1		
China clay	258	0,2	51,6		0,2	0,4
Flint	60	1,6	96			1,6
			Σ	1	0,2	2,0

The working recipe for the glaze will be:

Read lead	228,3 parts
China clay	51,6 -"-
Flint	96

/11/ Given the following lead frit formula, calculate a recipe using red lead, felspar, china clay, and flint:

$$\left.\begin{matrix}0,9\ PbO\\0,1\ K_2O\end{matrix}\right\}\ 0,3\ Al_2O_3\ ;\ 2,2\ SiO_2$$

Material	Molecular weight	Molecular parts	Parts by weight	PbO	K_2O	Al_2O_3	SiO_2
Read lead	685	0,9	$\frac{616,5}{3}=205,5$	0,9			
Felspar	556	0,1	55,6		0,1	0,1	0,6
China clay	258	0,2	51,6			0,2	0,4
Flint	60	1,2	72,0				1,2
			Σ	0,9	0,1	0,3	2,2

The working recipe for the glaze:

Read lead	205,5 parts
Felspar	55,6 -"-
China clay	51,6 -"-
Flint	72,0 -"-

/12/ Calculate the recipe for the frit of formula:

$$\left.\begin{array}{l}0{,}30\ Na_2O\\ 0{,}10\ K_2O\\ 0{,}60\ CaO\end{array}\right\}\ 0{,}18\ Al_2O_3\ \left\{\begin{array}{l}2{,}00\ SiO_2\\ 0{,}60\ B_2O_3\end{array}\right.$$

using borax, whiting, felspar, china clay, and flint.

In accordance with the Table **IV on the** p.87 materials to be used have following formulae and weights:

Borax $Na_2B_4O_7.10H_2O(382) \rightarrow Na_2O(62) + 2B_2O_3(2x70)$

Whiting $CaCO_3(106) \rightarrow CaO(56)$

Felspar $K_2O.Al_2O_3.6SiO_2(556) \rightarrow K_2O(94) + Al_2O_3(102) + 6SiO_2(6x60)$

China clay $Al_2O_3.2SiO_2.2H_2O(258) \rightarrow Al_2O_3(102) + 2SiO_2(2x60)$

Flint $SiO_2(60)$

Material	Molecular weight	Molecular parts	Parts by weight	Na_2O	K_2O	CaO	Al_2O_3	SiO_2	B_2O_3
Borax	382	0,3	114,6	0,3					0,6
Whiting	100	0,6	60,0			0,6			
Felspar	556	0,1	55,6		0,1		0,1	0,6	
China clay	258	0,08	20,6				0,08	0,16	
Flint	60	1,24	74,4					1,24	
			Σ	0,3	0,1	0,6	0,18	2,00	0,6

The working recipe for the frit, the formula of which is given above, will be as follows:

Borax	114,6	parts
Whiting	60,0	-"-
Felspar	55,6	-"-
China clay	20,6	-"-
Flint	74,4	-"-

VII Fritted Glazes

Most commercial glazes contain one or more frits. By fritting various components together it confers many desirable properties to the glaze.

The main reason for fritting are:

/1/ Soluble compounds, when fritted with other selected materials in the correct proportion, become insoluble. Glaze components should be insoluble, otherwise they tend to migrate into the pores of the biscuit ware and the glaze when fired may have a "starved" appearance.

/2/ Although lead compounds available to the ceramic industry are generally insoluble in water, they may have considerable solubility in dilute acids. If the compounds are soluble in dilute hydrochloric acid then they are toxic, since the gastric juices are highly acidic /0,17% hydrochloric acid/.

Lead compounds are fritted to produce glaze components which are virtually insoluble in dilute acids.

/3/ A glaze with a high proportion of clay substance may crack on drying. Chemically combined water has still to be released during the glost fire and these conditions may lead to a poor glost finish. Part of the plastic material should, therefore, be fritted, and part /approximately 10%/ used raw for glaze suspension.

/4/ Some compounds, such as calcium carbonate, liberate a gas on heating. Any compound that behaves in this way is fritted, so that the glaze is not likely to suffer from pin-holing and bubbling.

It is common practice to use two frits, i.e. a lead frit and a borax frit. If lead and B_2O_3 compounds are fritted together, then the lead does not generally reach satisfactory limits of insolubility. However, recent research has shown that lead borosilicate can be produced satisfactorily when the ratio of PbO : B_2O_3 is carefully selected.

Another point to consider is that the frit must mature at a reasonably low temperature. It follows then that the raw materials for a frit have to be selected to meet many requirements.

Experience has shown that the following limits, when applied to a frit, produce a product which has the necessary properties required for glaze manufacture. The basic to acidic oxide ratio should be within the range 1:1 to 1:3. Amphoteric to acidic oxide ratio 1:10 to 1:20.

Such compounds as CaO and MgO are often fritted with other materials to make them less soluble.

Synthesis of a Fritted Glaze

Oxides may be introduced into a fritted glaze in many forms. Some typical oxides are discussed below and the reasons stated for the choice of particular compounds.

K_2O. Compounds commercially available are: Pearl ash K_2CO_3, potassium nitrate KNO_3, potash felspar $K_2O.Al_2O_3.6SiO_2$ and stone. K_2O could be introduced by any of the above compounds. However, potash felspar is a likely choice; although it is insoluble and inert, it would introduce the required amounts of Al_2O_3 and SiO_2 to the frit.

Na_2O. Soda ash Na_2CO_3, borax $Na_2B_4O_7.10H_2O$, soda felspar $Na_2O.Al_2O_3.6SiO_2$ and stone. Since borax is cheap and a readily available compound and B_2O_3 is also required, then the Na_2O could be introduced into the frit as borax.

CaO. Invariably introduced as whiting /$CaCO_3$/ since this compound is extremely abundant and cheap.

PbO. Generally introduced as a lead bisilicate frit. Ideal formula $PbO.2SiO_2$.

Al_2O_3. Introduced as china clay $Al_2O_3.2SiO_2.2H_2O$. Part is put into the frit to give insolubility and some is left over for mill batch additions.

SiO_2. Introduced as flint /SiO_2/.

B_2O_3. Borax $Na_2B_4O_7.10H_2O$ is used wherever possible because of price and availability.

Fritting Factors

Consider the following frit:

Felspar	55,6 kg
Borax	95,5 kg
Whiting	35,0 kg
China clay	25,8 kg
Flint	42,0 kg
Total weight	253,9 kg

In practice, it is found that 253,9 kg of this frit recipe produce 189,9 kg of frit after heating.

The theoretical weight of frit produced can also be derived by calculation.

Felspar	55,6 x 1	-	55,6
Borax	95,5 x 0,529	-	50,5
Whiting	35,0 x 0,560	-	19,6
China clay	25,8 x 0,860	-	22,2

Flint 42,0 x 1 = $\frac{42,0}{189,9}$

The factors used above, e.g. borax 0,529, are referred to as "fritting factors".

Felspar has a fritting factor of 1 /one/ because it does not lose weight on heating.

Borax has a friting factor of 0,529. It is calculated as follows:

$$Na_2B_4O_7.10H_2O = \underbrace{Na_2O+2B_2O_3}+10H_2O$$

$$382 \equiv 202$$

$$1 \equiv \frac{202}{382} = 0,529$$

202 is the combined molecular weight of one molecule of Na_2O and two molecules of B_2O_3.

Whiting:

$$CaCO_3 = CaO+CO_2$$

$$100 \equiv 56$$

$$1 \equiv \frac{56}{100} = 0,56$$

Fritting factor = 0,56

China clay:

$$Al_2O_3.2SiO_2.2H_2O = \underbrace{Al_2O_3+2SiO_2}+2H_2O$$

$$258 \equiv 222$$

$$1 \equiv \frac{222}{258} = 0,86$$

Fritting factor = 0,86

A list of fritting factors for various compounds is given in Table IV on the p.87.

Typical analyses of ceramic materials are in Table V on p.87.

INTERNATIONAL ATOMIC WEIGHTS

Table II

Substance	Sym.	At. Wt.	Substance	Sym.	At. Wt.	Substance	Sym.	At. Wt.
Aluminium	Al	26·97	Helium	He	4.003	Radium	Ra	226·05
Antimony	Sb	121·76	Hlomium	Ho	164.94	Radon	Rn	222
Argon	A	39·944	Hydrogen	H	1.008	Rhenium	Re	186·31
Arsenic	As	74·91	Indium	In	114.76	Rhodium	Rh	102·91
Barium	Ba	137·36	Iodine	I	126.92	Rubidium	Rb	85·48
Beryllium	Be	9·02	Iridium	Ir	193.1	Ruthenium	Ru	101·7
Bismuth	Bi	209·00	Iron	Fe	55.85	Samarium	Sm	150·43
Boron	B	10·82	Kyrpton	Kr	83.7	Scandium	Sc	45·10
Bromine	Br	79·916	Lanthanum	La	138.92	Selenium	Se	78·96
Cadmium	Cd	112·41	Lead	Pb	207.21	Silicon	Si	28·06
Calcium	Ca	40·08	Lithium	Li	6.940	Silver	Ag	107·880
Carbon	C	12·010	Lutecium	Lu	174.99	Sodium	Na	22·997
Cerium	Ce	140·13	Magnesium	Mg	24.32	Strontium	Sr	87·63
Cesium	Cs	132·91	Manganese	Mn	54.93	Sulphur	S	32·06
Chlorine	Cl	35·457	Mercury	Hg	200.61	Tantalum	Ta	180·88
Chromium	Cr	52·01	Molybdenum	Mo	95.95	Tellurium	Te	127·61
Cobalt	Co	58·94	Neodymium	Nd	144.27	Terbium	Tb	159·2
Columbium	Cb	92·91	Neon	Ne	20.183	Thallium	Tl	204·39
Copper	Cu	63·57	Nickel	Ni	58.69	Thorium	Th	169·4
Dysprosium	Dy	162·46	Nitrogen	N	14.008	Tin	Sn	118·70
Erbium	Er	167·2	Osmium	Os	190.2	Titanium	Ti	47·90
Europium	Eu	152·0	Oxygen	O	16.000	Tungsten	W	183·92
Fluorine	F	19·00	Palladium	Pd	106.7	Uranium	U	238·07
Gadolinum	Gd	156·9	Phosphorus	P	30.98	Vanadium	V	50·95
Gallium	Ga	69·72	Platinum	Pt	195.23	Xenon	Xe	131·3
Germanium	Ge	72·60	Potassium	K	39.096	Ytterbium	Yb	173·04
Gold	Au	197·2	Praseodymium	Pr	140.92	Yttrium	Y	88·92
Hafnium	Hf	178·6	Protactinium	Pa	231	Zinc	Zn	65·38
						Zirconium	Zr	91·22

TABLE OF MINERALS

Table III

Name	Description	Formula
Agate	A form of crystalline silica	SiO_2
Albite	Soda felspar	$Na_2O.Al_2O_3.6SiO_2$ $[Na.Al.Si_3O_8]$
Amphiboles	Silicates with chains of silicon-oxygen linkages	$n(Si_4O_{11})^{6-}$
Anatase	A natural form of titanium dioxide	TiO_2
Anhydrite	Anhydrous calcium sulphate	$CaSO_4$
Anorthite	Lime-felspar	$CaO.Al_2O_3.2SiO_2$ $[Ca.Al_2.Si_2O_8]$
Apatite	Halogen derivative of calcium phosphate	$Ca_3(Cl.F.OH)(PO_4)_3$
Aragonite	A natural form of calcium carbonate	$CaCO_3$
Baddeleyite	A naturally occurring zirconia mineral	
Barytes	Heavy spar. Barium sulphate	$BaSO_4$
Bauxite	A natural form of hydrated alumina	$Al_2O_3.2H_2O$
Bentonite	An extremely fine grained montmorillonite type of clay	
Beryl	An example of the ring structure silicates	$3BeO.Al_2O_3.6SiO_2$ $[Be_3Al_2Si_6O_{18}]$
Boracite	A naturally occurring borate mineral	$6MgO.MgCl_2.8B_2O_3$
Borocalcite	Natural form of calcium diborate	$CaO.2B_2O_3.6H_2O$
Brookite	A natural form of titania	TiO_2
Calcite	A natural form of calcium carbonate	$CaCO_3$
Carborundum	A synthetic compound of silicon carbide	SiC
Chert	Chalcedonic silica	SiO_2
China clay	A primary clay essentially kaolinite	$Al_2O_3.2SiO_2.2H_2O$ $[Al_2(OH)_4(Si_2O_5)]$
Chromite	A chrome mineral of the spinel group	$FeO.Cr_2O_3$
Cobaltite	A sulphide containing cobalt and arsenic	$Co.As.S$
Corundum	A crystalline form of alumina	Al_2O_3
Cristobalite	Highest temperature form of crystalline silica	SiO_2
Cryolite	Mineral sodium aluminium fluoride	Na_3AlF_6
Dolomite	A double salt of calcium magnesium carbonate	$CaCO_3.MgCO_3$
Felspar	See orthoclase, albite and anorthite	
Flint	Crypto-crystalline chalcedonic silica	SiO_2
Fluorspar	Calcium fluoride	CaF_2
Fullers Earth	Clay similar to bentonite with high absorbing powers	
Galena	Natural lead sulphide	PbS
Ganister	A fine grained quartz rock	SiO_2
Gypsum	Calcium sulphate dihydrate	$CaSO_4.2H_2O$
Haematite	A naturally occurring form of iron oxide	Fe_2O_3
Iceland Spar	See calcite	
Iron Pyrites	Iron sulphide	FeS_2
Kaolinite	Clay substance	$Al_2O_3.2SiO_2.2H_2O$ $[Al_2(OH)_4(Si_2O_5)]$
Kieselguhr	Diatomaceous earth; remains of the diatom animal	SiO_2
Kyanite	An alumino-silicate	$Al_2O_3.SiO_2$
Lepidolite	A micaceous form of lithium mineral	$(Li.K.Na)_2(F.OH)_2$ $Al_2O_3.3SiO_2$
Lignite	A low-grade brown coal	60–70% carbon
Limonite	Hydrated iron oxide	$Fe_2O_3.xH_2O$
Magnesite	A naturally occurring form of magnesium carbonate	$MgCO_3$
Magnetite	Magnetic iron oxide	Fe_3O_4
Marcasite	Ferrous sulphide	FeS_2
Mica	See muscovite	
Montmorillonite	A type of clay substance	$Na.Al_5.Mg.Si_{24}.O_{60}.(OH)_{12}$
Mullite	A crystalline constituent of some fired bodies	$3Al_2O_3.2SiO_2$
Muscovite	Potash mica	$K_2O.3Al_2O_3.6SiO_2.2H_2O$
Nepheline	A low silica flux	$3(Na_2O).K_2O$ $[4Al_2O_3.8SiO_2]$
Nepheline Syenite	A rock consisting of nepheline and felspar	
Thivier's Earth	A clay high in iron oxide	
Tourmaline	A complex boro-silicate of Al and Na, plus traces of Li, Fe und Mg	
Tremolite	A calcium magnesium silicate. Amphibole type	$CaO.3MgO.4SiO_2$
Tridymite	An intermediate crystalline form of silica	SiO_2
Vermiculite	Hydrous mica	$3MgO.(Fe.Al)_2O_3.3SiO_2$
Willemite	Zinc silicate of the olivine type	$2ZnO.SiO_2$
Witherite	A natural form of barium carbonate	$BaCO_3$
Wollastonite	Calcium metasilicate	$CaO.SiO_2$
Whiting	Calcium carbonate	$CaCO_3$
Zircon	Zirconium silicate	$ZrO_2.SiO_2$
Zirconia	Zirconium oxide	ZrO_2

Table IV

COMPOUNDS USED IN GLAZE CALCULATIONS WITH THEIR PERMANENT OXIDES AND FRITTING FACTORS

The approximate molecular weights that are commonly used are shown in brackets.

Compound and Fritting Factor		Formulae and Molecular Weights
Borax	0·529	$Na_2B_4O_7.10H_2O.(382) \rightarrow Na_2O(62) + 2B_2O_3(2 \times 70)$
Boric acid	0·564	$2H_3BO_3(2 \times 62) \rightarrow B_2O_3(70)$
China clay	0·861	$Al_2O_3.2SiO_2.2H_2O.(258) \rightarrow Al_2O_3(102) + 2SiO_2(2 \times 60)$
Felspar	1·00	$K_2O.Al_2O_3.6SiO_2(556) \rightarrow K_2O(94) + Al_2O_3(102) + 6SiO_2(6 \times 60)$
Flint	1·00	$SiO_2(60)$
Lead bisilicate	1·00	$PbO.2SiO_2.(343) \rightarrow PbO(223) + 2SiO_2(2 \times 60)$
Pearl ash	0·681	$K_2CO_3(138) \rightarrow K_2O(94)$
Red lead	0·977	$Pb_3O_4(685) \rightarrow 3PbO(3 \times 223)$
Soda ash	0·585	$Na_2CO_3(106) \rightarrow Na_2O(62)$
Whiting	0·560	$CaCO_3(100) \rightarrow CaO(56)$
White lead	0·863	$Pb(OH)_2.2PbCO_3(775) \rightarrow 3PbO(3 \times 223)$

Table V

TYPICAL ANALYSES OF CERAMIC MATERIALS

	Alumina brick	Black ball clay	Blue ball clay	Bone ash	China clay	Chrome ore	Dolomite
SiO_2	13·73	46·86	50·56	0·31	47·00	2·10	0·24
TiO_2	2·88	0·68	0·87		0·10	0·21	
Al_2O_3	81·54	34·80	33·40	0·06	37·05	16·45	0·10
Fe_2O_3	1·41	0·80	1·25	0·13	0·59	16·50	0·05
MgO	0·10	0·32	0·40	1·26	0·28	16·26	21·20
CaO	0·11	0·32	0·59	54·26	0·15	0·12	31·20
K_2O	0·36	1·47	3·10		1·78	0·01	0·07
Na_2O	0·11	0·30	0·64	0·34	0·30	0·18	0·13
Loss	0·14	14·30	9·66	1·38	12·55	1·02	47·47
P_2O_5				42·12			
Cr_2O_3						46·70	

	E'thware body	Felspar	Flint	Fireclay brick	Molochite	Pegmatite	Plaster
SiO_2	69·93	68·00	97·97	55·27	54·81	72·23	0·54
TiO_2	0·01	0·02	0·01	1·04	0·10	0·03	0·02
Al_2O_3	19·53	16·85	0·39	35·30	42·31	17·83	0·14
Fe_2O_3	0·63	0·18	0·06	4·94	0·75	0·28	0·06
MgO	0·07	0·13	0·05	1·16	0·12	0·12	0·30
CaO	0·73	0·37	0·62	0·37	0·20	0·90	38·59
K_2O	1·60	10·64	0·02	1·63	1·73	1·90	0·03
Na_2O	0·62	2·58	0·04	0·39	0·11	5·96	0·08
Loss	5·75	0·41	0·65	0·34		0·53	7·88
SO_3							52·51

	Sand	Silica brick	Slate	Red clay	Stone	Whiting
SiO_2	95·02	95·90	51·54	37·68	72·76	0·04
TiO_2	0·13	0·17	0·94	0·52	0·05	
Al_2O_3	2·07	0·85	19·63	12·51	15·36	0·11
Fe_2O_3	0·21	0·79	8·26	5·00	0·16	0·01
MgO	0·12	0·06	1·99	1·94	0·16	0·04
CaO	0·15	1·75	1·44	19·34	1·57	56·06
K_2O	0·91	0·12	3·20	2·75	4·33	
Na_2O	0·16	0·08	1·31	0·25	3·17	0·03
Loss	0·37		5·08	20·12	1·93	43·83
SO_3						0·30
Cl						0·02

B.

VIII. Heat transfer

Heat transfer is another basic phenomena in the manufacturing of ceramics which has to be dealt with.

Heat is always transmitted from places of higher temperature to places of lower temperature. There are three fundamental modes of heat transfer:

a/ by conduction - as a rule in solids ;

b/ by convection - as a rule in liquids or gases ;

c/ by radiation - in transparent media.

When calculating the parameters of ceramic furnaces all three modes of heat transmission must be considered. Conduction should be normally taken into account to calculate thermal losses through the walls, convection as the primary mode of heat transmission in gases in the furnace, while radiation comes into consideration for the heat transmission from the combustion products and furnace walls into the fired ceramic body.

Conduction

Conduction in a homogeneous opaque solid is the transfer of heat from one part to another, under the influence of a temperature gradient, without appreciable displacement of the particles. Conduction involves the transfer of kinetic energy from one molecule to an adjacent molecule; it is the only mechanism of heat flow in an opaque solid. With gases and liquids, convection may be supplemented by convection and radiation. Within a fluid flowing in streamline motion, heat is transferred by conduction at right angles to the direction of fluid flow.

Convection

Convection involves the transfer of heat by mixing one parcel of fluid with another. The motion of the fluid may be entirely the result of differences of density resulting from the temperature differences, as in natural convection, or the motion may be produced by mechanical means, as in forced convection.

Radiation

A hot body emits radiant energy in all directions. When this energy strikes another body, part may by reflected. Part may be transmitted through the body, in which case the body is said to be diathermanous. The remainder is absorbed and quantitatively transformed into heat.

VIII a/ Transmission of heat by conduction

Transient conduction is a very complex process, which in many cases cannot be mastered mathematically. What we can solve are only simpler cases, which are however of very great interest to us in the calculations for furnaces. We presume that we are confronted with transmissions of heat in isotropic media, i.e. media exhibiting the same physical properties in all directions. The thermal state of such a medium is given by the temperature field, i.e. a set of momentary temperatures at all the points of the portion of space under consideration. The temperature field is continuous, uninterrupted and scalar. The surfaces including points of equal temperature are termed isothermal surfaces. If we are dealing with simple one-dimensional heat transfer through a wall, the isothermal surfaces are parallel with the interface. In the case of a straght wall we are therefore concerned with planar surfaces, in the case of a cylindrical surface with co-axial cylinders, in the case of a spherical surface with concentric spheres, and so on.

Lines connecting points of equal temperatures /see Fig. 2 /

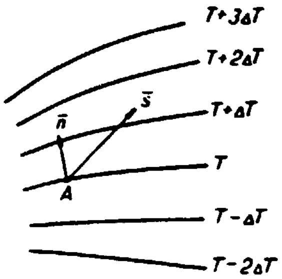

Fig.2. Pattern of isotherms and direction of heat flow vector

are called isotherms. When travelling along the isotherm T from A is the direction $\bar{s}$ we reach points with different temperatures. Travel in the direction $\bar{s}$ is characterized by the ratio

$$\frac{\Delta T}{\Delta \bar{s}}$$

which will be a maximum if the motion takes place in the direction of normal $\bar{n}$, i.e. a normal to isotherm T. The temperature gradient

$$\text{grad } T$$

is the limiting value of the ratio $\frac{\Delta T}{\Delta \bar{n}}$ or

$$\text{grad } T = \lim_{\Delta \bar{n} \to 0} \frac{\Delta T}{\Delta \bar{n}} \bar{n}_o \qquad /35/$$

where $\bar{n}_o$ is the unit vector

$$\text{grad } T = \frac{\partial T}{\partial \bar{n}} \bar{n}_o \ [\mathrm{K\ m^{-1}}] \qquad /36/$$

The temperature gradient is a vector perpendicular to the isothermal surface. Resolving the general direction $\bar{n}$ into components in the direction of the co-ordinates, the following will apply:

$$\text{grad } T = \frac{\partial T}{\partial x} \bar{i} + \frac{\partial T}{\partial y} \bar{j} + \frac{\partial T}{\partial z} \bar{k} \qquad /37/$$

where $\bar{i}, \bar{j}, \bar{k}$ are unit vectors in the direction of the axes x,y and z.

Grad T is positive in the direction of increase of the temperature, but heat flows in the opposite direction.

The set of temperature gradients constitutes a vector field. The existence of a vector field signifies that heat is being transmitted within the medium.

The relationship between the heat flux, the temperature gradient and the properties of the medium are described by Fourier's law:

$$d\bar{Q} = -\lambda \frac{\partial T}{\partial \bar{n}} dF\, dt \quad [J] \qquad /38/$$

$d\bar{Q}$ is the amount of heat transported in the direction normal to area dF of isothermal surface in time dt. It depends on a physical property of the medium, the coefficient of thermal conductivity λ and temperature gradient $\frac{\partial T}{\partial \bar{n}}$. The minus sign implies that the heat flows from higher temperatures to the lower ones. Since grad T is a vector, $d\bar{Q}$,too, will be a vector.

The heat flux density $\bar{q}$ is the flux traversing a unit area in a unit of time

$$\bar{q} = -\lambda \frac{\partial T}{\partial \bar{n}} \quad [W\, m^{-2}] \qquad /39/$$

or

$$\bar{q} = \frac{\bar{Q}}{Ft} \quad [W\, m^{-2}] \qquad /40/$$

Vector $\bar{q}$ can be resolved into the directions of the axes of the co-ordinates:

$$\bar{q} = -\lambda\left(\frac{\partial T}{\partial x}\bar{i} + \frac{\partial T}{\partial y}\bar{j} + \frac{\partial T}{\partial z}\bar{k}\right) \qquad /41/$$

The dimension of thermal conductivity λ is $[Wm^{-1}K^{-1}]$.
The thermal conductivity is the amount of heat transported through 1 sq.metre of isothermal surface within a time unit, with a thermal gradient of 1 degree K or C per 1 metre of

thickness. It is a property related to composition and must be determined for each substance. It varies within wide limits.

The thermal conductivity of metals decreases as temperature rises, but for silicates as temperature rises thermal conductivity on the contrary increases. The temperature dependence is normally linear, and can be expressed by the relationship

$$\lambda_T = \lambda_O\left(1 + bT\right) \qquad /42/$$

With porous materials, thermal conductivity also depends on other conditions such as humidity, specific gravity or bulk density and structure.

Thermal conductivity of metals

The values are high and proportional to their electrical conductivities. Thermal conductivities of alloys are lower than those of pure metals.

Silver possesses the highest thermal conductivity /420 $Wm^{-1}K^{-1}$/, followed by pure electrolytic copper /380 $Wm^{-1}K^{-1}$/, then gold /250 $Wm^{-1}K^{-1}$/ and aluminium /230 $Wm^{-1}K^{-1}$/. The thermal conductivity of Mo is 145 /$Wm^{-1}K^{-1}$/ that of Pt, 73/$Wm^{-1}K^{-1}$/. The conductivity of ferrous alloys is much influenced by the carbon content; structural steel and cast iron have thermal conductivities about 50 /$Wm^{-1}K^{-1}$/ at room temperature. Rather low thermal conductivities are typical of nickel or chromium-alloyed steels /12 to 16 $Wm^{-1}K^{-1}$/.

Thermal conductivities of refractory materials

These are in the range of tenths up to units /$Wm^{-1}K^{-1}$/, and as the temperature increases, their values usually increase moderately.

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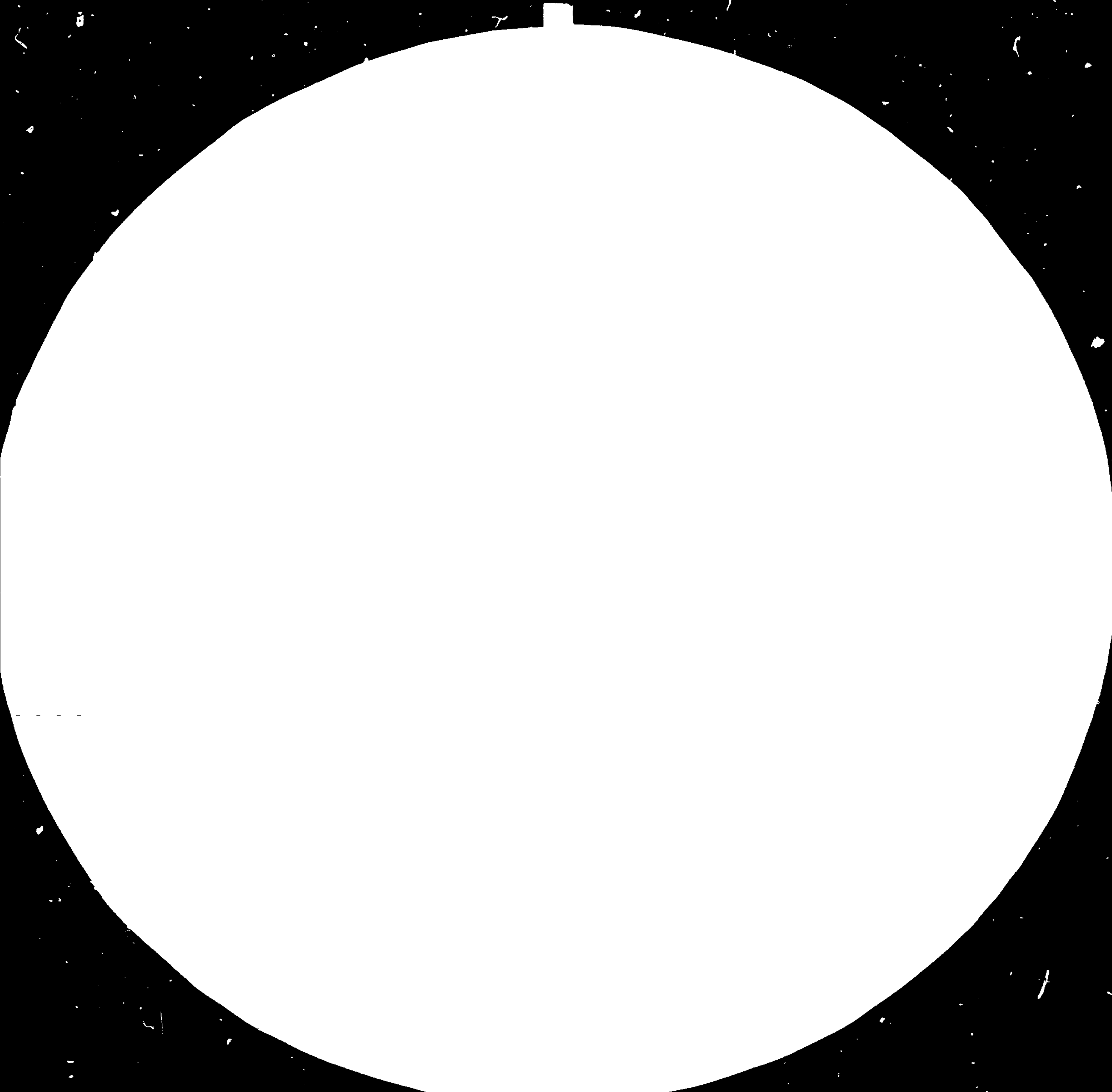

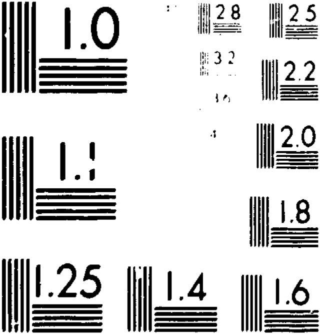

MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF STANDARDS-1963-A

With some materials thermal conductivity can be determined from empirical formulae.

Empirical formulae for the calculation of thermal conductivities in $/Wm^{-1}K^{-1}/$ of some refractory and building materials are given in Table VI

Table VI

Material	Bulk density ϱ_V [kg m^{-3}]	T [°C] Thermal conductivity λ [W m^{-1} K^{-1}]
Dense fireclay	1800 to 2200	$0.7 + 0.64 \times 10^{-3} \times T$
Dense silica	1700 to 2000	$0.84 + 0.76 \times 10^{-3} \times T$
Fireclay highi n Al_2O_3	3000	$1.69 - 0.23 \times 10^{-3} \times T$
Mullite	2160 to 2900	$2.29 + 1.7 \times 10^{-3} \times T$
Zircon		$1.3 + 0.64 \times 10^{-3} \times T$
Magnesite	2600 to 2700	$6.17 - 2.68 \times 10^{-3} \times T$
Chrome magnesite	2900 to 3000	2.1 to 4.1
Silicon carbide	2100 to 2500	$9.3 + 1.75 \times 10^{-3} \times T$
Red brick	1750 to 2100	$0.47 + 0.51 \times 10^{-3} \times T$
Concrete	2400	0.92
Light-weight fireclay	810 to 1340	0.175 to 0.33
Light-weight silica	690 to 1000	0.256 to 0.48
Asbestos board	900 to 1200	$0.157 + 0.14 \times 10^{-3} \times T$
Crushed asbestos	800	$0.106 + 0.18 \times 10^{-3} \times T$

Thermal conductivity of liquids

It normally varies within the range λ = 0,1 to 0,7 $/Wm^{-1}K^{-1}/$. With the increase of temperature, λ decreases, with the exception of water and anhydrous glycerine.

Thermal conductivity of gases

The thermal conductivity usually varies within the range of λ = 0,006 to 0,6 $/Wm^{-1}K^{-1}/$. Those having higher densities possess lower thermal conductivities. Only under high vacuum - below 6,5 /Pa/- does thermal conductivity depend markedly on pressure - otherwise it is independent of it.

General solution of the differential equation of heat conduction /Fourier-Kirchhoff equation/

Let a homogeneous and isotropic body be unevenly heated. The walls of the elementary prism dx dy dz /Fig. 3 / will have different temperatures. According to the Fourier equation, the amount of heat entering area A will be:

$$dQ_A = -\lambda \frac{\partial T}{\partial z} dx\, dy\, dt \qquad /43/$$

and the heat leaving at a distance dz the area B having a generally different temperature $T + \frac{\partial T}{\partial z}.dz$ shall be, again under Fourier's equation:

$$dQ_B = -\lambda\, dx\, dy \frac{\partial}{\partial z} \left(T + \frac{\partial T}{\partial z} dz \right) dt \qquad /44/$$

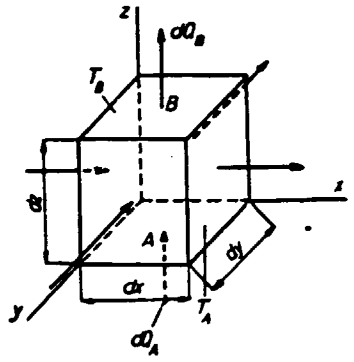

Fig.3. Heat transfer by conduction in an elementary parallelepiped

Assuming that $T_A > T_B$, the heat will travel in the direction from A to B, a part of it remaining in the body and causing the body itself to be heated. The amount of heat dQ that will remain in the body will be :

$$
\begin{aligned}
dQ_1 &= dQ_A - dQ_B = \\
&= -\lambda\, dx\, dy \frac{\partial T}{\partial z} dt - \left[-\lambda\, dx\, dy \frac{\partial}{\partial z}\left(T + \frac{\partial T}{\partial z} dz \right) dt \right] = \\
&= \lambda\, dx\, dy\, dt \left[-\frac{\partial T}{\partial z} + \frac{\partial}{\partial z}\left(T + \frac{\partial T}{\partial z} dz \right) \right] = \\
&= \lambda\, dx\, dy\, dz \frac{\partial^2 T}{\partial z^2} dt
\end{aligned}
\qquad /45/
$$

Analogous expressions can be written for the heat flow in the x and y directions.

The overall rise in temperature of the elementary prism will be given by the addition of increments of temperatures caused by the heat flux in the directions x,y and z.

$$dQ = \lambda\left(\frac{\partial^2 T}{dx^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) dx\ dy\ dz\ dt \qquad /46/$$

Due to this heat the body is reheated in time dt by the value of

$$\frac{\partial T}{\partial t} \cdot dt$$

If density of the body be ρ and the specific heat c, then to heat the body by the above value /2,18/ the following heat will be consumed

$$dQ = dx\ dy\ dz c\rho\ \frac{\partial T}{\partial t}\ dt \qquad /47/$$

Deducting /47/ from /46/, we shall obtain:

$$0 = \lambda\left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) dx\ dy\ dz\ dt - dx\ dy\ dz c\rho\ \frac{\partial T}{\partial t}\ dt$$

Defining the group

$$\frac{\lambda}{c\rho} = a \qquad /48/$$

the thermal diffusivity, we obtain:

$$\frac{\partial T}{\partial t} = a\left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2}\right) \qquad /49/$$

The group of derivatives

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \nabla^2 \qquad /50/$$

is the Laplace differential operator, so that

$$\frac{\partial T}{\partial t} = a\nabla^2 T \qquad /51/$$

Eqs. /49/,/51/ express the mutual relationship between the distribution in time and space of the temperatures at an arbitrary point of the body in which heat is being transferred.

The coefficient of proportionality $\underline{a}$ is thermal diffusivity, and expresses the rate of change of temperatures in transient conduction of heat. Its dimensions are

$$a = \frac{\lambda}{c\rho} \; ; \quad [a] = \frac{W\ m^{-1} K^{-1}}{J\ kg^{-1} K^{-1} kg\ m^{-3}} = [m^2 s^{-1}]$$

If thermal conductivity λ expresses the ability of matter to conduct heat, diffusivity $\underline{a}$ expresses the thermal inertia of the matter. It is likewise related to composition. It is low for gases and liquids and high for metals. Values $\underline{a}$ of some of the substances are given in the table below. /VII/

Table VII

THERMAL DIFFUSIVITIES *a* OF VARIOUS SUBSTANCES

Material	*a* [cm^2 s^{-1}]	Material	*a* [cm^2 s^{-1}]	Material	*a* [cm^2 s^{-1}]
Silver	1.71	Granite	0.011	Wood	
Copper	1.14	Limestone	0.007	(along annual rings)	0.004 5
Aluminium	0.86	Sandstone	0.011	Wood	
Zinc	0.41	Glass	0.0058	(normal to rings)	0.002 4
Tin	0.38	Concrete	0.0042	Cork	0.001 4
Brass	0.33	Brick	0.0038	Dense fireclay	0.001 6363
Platinum	0.25	Dry sand	0.0020	Porous fireclay	0.000 808
Steel	0.12	Moist sand	0.0033	Dense silica	0.001 57
Cast iron	0.12	(8%)		Fused cast material	0.002 3
				Diatomaceous earth	0.000 857

In a steady-state heat transfer problem

$$\frac{\partial T}{\partial t} = 0$$

hence

$$a \,.\, \nabla^2 T = 0 \qquad /52/$$

Eq./52/will assume the form

$$\nabla^2 T = 0 \qquad /53/$$

seeing that $a \neq 0$.

Eq./53/ has a great number of possible solutions, any particular solution depends on the boundary conditions. The functions that satisfy the equation for the steady state yield isothermal surfaces which do not change their positions.

Heat conduction through a simple planar wall

The simplest solution is one for a one-dimensional heat flow, for example with infinitely large flat slabs, with heat flow perpendicular to the surface, or radially in a cylinder of infinite length, or in a sphere.

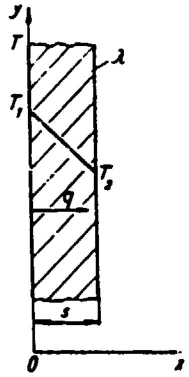

Fig.4. Heat conduction through a simple planar wall

In the case shown in Fig. 4 heat is transmitted in the direction of axis x, this implying that the surface y,z are isotherms, hence

$$\frac{\partial T}{\partial y} = \frac{\partial T}{\partial z} = 0$$

The differential equation /53/ will be simplified to the form

$$\frac{d^2T}{dx^2} = 0 \qquad /54/$$

The axes shall be selected in the manner shown in Fig. 4 so that for

$$x = 0 , \quad T = T_1$$

and

$$x = s , \quad T = T_2 \qquad /55/$$

Eq./54/ is solved by integration: after the first integration

$$\frac{dT}{dx} = C_1 \qquad /56/$$

and after the second

$$T = C_1x + C_2 \qquad /57/$$

Constants C_1 and C_2 must be determined from boundary conditions /55/

$$C_2 = T_1$$

$$C_1 = - \frac{T_1-T_2}{s} \qquad /58/$$

substituting

$$T = T_1 - \frac{T_1-T_2}{s}\, x \qquad /59/$$

If we are only to establish the difference in temperatures $\Delta T_o = T_1-T_2$, it is convenient to convert the equation to a dimensionless form, by introducing

$$\Delta T = T-T_2 \quad \text{and} \quad \Delta T_o = T_1-T_2$$

then by substituting in/59/ we will obtain

$$T-T_2 = T_1-T_2- \frac{T_1-T_2}{s}\, x$$

$$\Delta T = \Delta T_o - \frac{\Delta T_o}{s} x$$

$$\frac{\Delta T}{\Delta T_o} = 1 - \frac{x}{s} \qquad /60/$$

Denoting

$\frac{\Delta T}{\Delta T_o} = \theta$ as a dimensionless temperature

and

$\frac{x}{s} = X$ as dimensionless distance,

then

$$\theta = 1 - X \qquad /61/$$

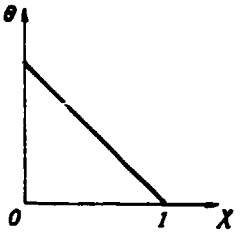

Fig.5. Relationship between dimensionless temperature distribution and wall thickness

Equation /61/ is a universal equation of a dimensionless temperature field in a thin wall /see Fig. 5 /. It illustrates the temperature distribution in a wall of thickness s, and boundary temperatures T_1 and T_2.

The amount of heat traversing a unit area in a unit of time is determined from Fourier's equation

$$q = -\lambda \frac{\partial T}{\partial x} \qquad /39/$$

because

$$\frac{\partial T}{\partial x} = C_1 = - \frac{T_1 - T_2}{s} \qquad \text{/see / 56 /,/ 58 /}$$

after substituting /39/ becomes

$$q = \frac{\lambda}{s} (T_1 - T_2) \quad [Wm^{-2}] \qquad /62/$$

The equation can be rewritten in the form

$$\frac{q}{\lambda} = \frac{T_1 - T_2}{s} \qquad /63/$$

Substituting this expression into equation for the temperature field / 59 /, we obtain

$$T_x = T_1 - \frac{q}{\lambda} x \qquad /64/$$

From this it follows that under otherwise equal conditions, an increase in temperature difference between the surfaces means an increase in the heat flux q.

The total amount of heat flowing through a wall having the area F m^2 in time t /hrs/ will be

$$Q = qFt = \frac{\lambda}{s}\left(T_1 - T_2\right) Ft \quad \left[J\right] \qquad /65/$$

The expression $\frac{\lambda}{s}\left[Wm^{-2}K^{-1}\right]$ is referred to as thermal conductivity of the wall, its reciprocal value $\frac{s}{\lambda}\left[m^2KW^{-1}\right]$ being termed thermal resistance of the wall.

Steady conduction of heat through a composite planar wall

The wall consists of n homogeneous layers /see Fig. 6 /, each of which has a different thermal conductivity $\lambda_1, \lambda_2, \lambda_3 \ldots \lambda_n$. We assume contact between the layers to be perfect, and each material to have the same interface temperature. If the temperatures of the surfaces of the wall T_1 and T_{n+1} are given, then at steady state the flow through unit area per unit of time will be equal through all isothermal surfaces. We can write a system of equations /62/ :

$$\begin{aligned} q &= \frac{\lambda_1}{s_1}(T_1 - T_2) \\ q &= \frac{\lambda_2}{s_2}(T_2 - T_3) \\ q &= \frac{\lambda_3}{s_3}(T_3 - T_4) \\ &\vdots \\ q &= \frac{\lambda_n}{s_n}(T_n - T_{n+1}) \end{aligned} \qquad /66/$$

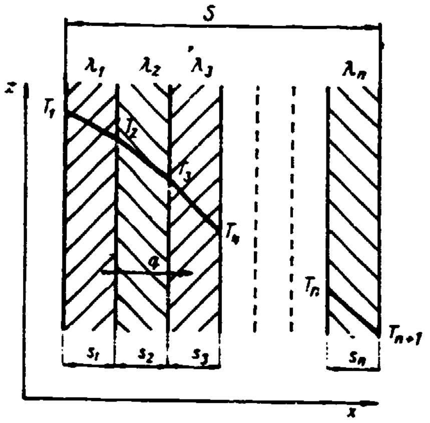

Fig.6. Heat conduction through a composite flat wall

From them we can determine the temperature gradients in the individual layers of the wall:

$$T_1 - T_2 = q\frac{s_1}{\lambda_1}$$

$$T_2 - T_3 = q\frac{s_2}{\lambda_2}$$

$$T_3 - T_4 = q\frac{s_3}{\lambda_3}$$

$$\vdots$$

$$T_n - T_{n+1} = q\frac{s_n}{\lambda_n} \qquad /67/$$

By summing up these equations we obtain:

$$T_1 - T_{n+1} = q\left(\frac{s_1}{\lambda_1} + \frac{s_2}{\lambda_2} + \frac{s_3}{\lambda_3} + \dots + \frac{s_n}{\lambda_n}\right)$$

from which

$$q = \frac{T_1 - T_{n+1}}{\frac{s_1}{\lambda_1} + \frac{s_2}{\lambda_2} + \frac{s_3}{\lambda_3} + \dots + \frac{s_n}{\lambda_n}} = \frac{T_1 - T_{n+1}}{\sum_{i=1}^{i=n}\frac{s_i}{\lambda_i}} \quad [\mathrm{W\,m^{-2}}] \qquad /68/$$

The expression $\sum_{i=1}^{i=n} \frac{s_i}{\lambda_i}$ is the sum of thermal resistances of all the layers of the wall. The temperatures on the interfaces of individual layers are computed from Eqs. /67/

$$T_2 = T_1 - q\frac{s_1}{\lambda_1}$$

$$T_3 = T_2 - q\frac{s_2}{\lambda_2} = T_1 - q\left(\frac{s_1}{\lambda_1} + \frac{s_2}{\lambda_2}\right) \qquad /69/$$

Generally

$$T_{k+1} = T_1 - q\sum_{i=1}^{i=k}\frac{s_i}{\lambda_i} \quad [^\circ\mathrm{C}] \qquad /70/$$

Steady radial conduction of heat through a simple cylindrical wall

Let us consider a tube of length l ; the inner surface of the wall having radius r_1 and temperature T_1, the outer surface having radius r_2 and temperature T_2. We assume that the material of the tube has a constant thermal conductivity λ independent of temperature, and heat is conducted radially - see Fig.7 The isothermal surfaces are cylindrical, co-axial with the cylinder surface. The heat that traverses this cylindrical surface of radius r and length l in unit time will be, according to Fourier's law,

$$Q = -\lambda F \frac{\mathrm{d}T}{\mathrm{d}r} = -2\pi r l \frac{\lambda\, \mathrm{d}T}{\mathrm{d}r} \quad [\mathrm{W}] \qquad /71/$$

$$\mathrm{d}T = -\frac{Q}{2\pi\lambda l}\frac{\mathrm{d}r}{r}$$

$$T = -\frac{Q}{2\pi\lambda l}\ln r + \mathrm{C} \qquad /72/$$

If we integrate over the range from T_1 to T_2 and r_1 to r_2

$$\int_{T_1}^{T_2} \mathrm{d}T = -\frac{Q}{2\pi\lambda l}\int_{r_1}^{r_2}\frac{\mathrm{d}r}{r}$$

$$T_1 - T_2 = \frac{Q}{2\pi\lambda l}\ln\frac{r_2}{r_1} \qquad /73/$$

Hence the heat being transmitted

$$Q = \frac{2\pi\lambda l}{\ln\frac{r_2}{r_1}}(T_1 - T_2) = \frac{2\pi\lambda l}{\ln\frac{d_2}{d_1}}(T_1 - T_2) \quad [\mathrm{W}] \qquad /74/$$

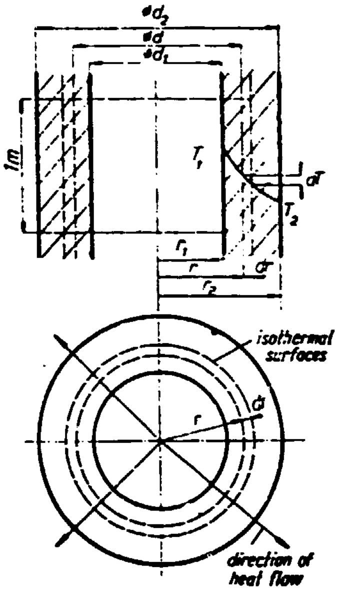

Fig.7. Heat conduction through a simple cylindrical wall

The equation of the temperature distribution in the wall will be established by determining constant C from the boundary conditions, and introducing in into Eq. /72/

For radius r_1 the temperature of the wall will be T_1, and the constant

$$C = T_1 + \frac{Q}{2\pi\lambda l} \ln r_1$$

By substituting into /72/ we obtain

$$T = -\frac{Q}{2\pi\lambda l}\ln r + T_1 + \frac{Q}{2\pi\lambda l}\ln r_1 = T_1 - \frac{Q}{2\pi\lambda l}\ln\frac{d}{d_1}$$

For Q we shall substitute from /74/

$$T = T_1 - \frac{2\pi\lambda l}{\ln\frac{d_2}{d_1}}(T_1 - T_2)\frac{1}{2\pi\lambda l}\ln\frac{d}{d_1} = T_1 - (T_1 - T_2)\frac{\ln\frac{d}{d_1}}{\ln\frac{d_2}{d_1}} \qquad /75/$$

The temperature in the wall of the tube will vary in accordance with the logarithmic curve. The amount of heat transmitted through 1 m length of the tube will be

$$q = \frac{Q}{l} = \frac{2\pi\lambda}{\ln\frac{d_2}{d_1}}(T_1 - T_2) \quad [\mathrm{W\,m^{-1}}] \qquad /76/$$

Steady conduction of heat through a composite cylindrical wall

/Fig. 8 /.

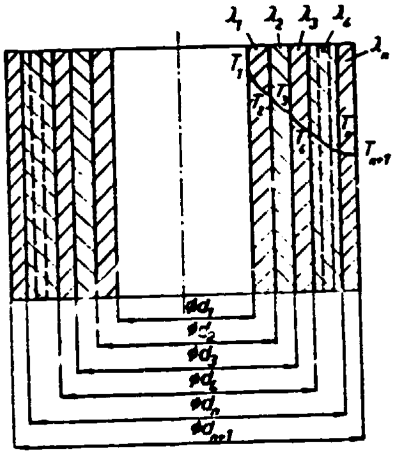

Fig.8. Heat conduction through a composite cylindrical wall

The dimension of the tubes diameter d_1 ... diameter d_{n+1}, thermal conductivities of the materials λ_1, ... λ_n, and the temperatures of the inner and outer surfaces T_1 and T_{n+1} are known. The following amount of heat will pass through the isothermal surfaces:

$$q = \frac{Q}{l} = \frac{2\pi(T_1 - T_2)}{\frac{1}{\lambda_1}\ln\frac{d_2}{d_2}} = \frac{2\pi(T_2 - T_3)}{\frac{1}{\lambda_2}\ln\frac{d_3}{d_2}} = \dots = \frac{2\pi(T_n - T_{n+1})}{\frac{1}{\lambda_n}\ln\frac{d_{n+1}}{d_n}}\,[\mathrm{W\,m^{-1}}] \qquad /77/$$

From which we shall determine:

$$\begin{aligned} T_1 - T_2 &= \frac{q}{\pi}\frac{1}{2\lambda_1}\ln\frac{d_2}{d_1} \\ T_2 - T_3 &= \frac{q}{\pi}\frac{1}{2\lambda_2}\ln\frac{d_3}{d_2} \\ &\vdots \\ T_n - T_{n+1} &= \frac{q}{\pi}\frac{1}{2\lambda_n}\ln\frac{d_{n+1}}{d_n} \end{aligned} \qquad /78/$$

By summing up these equations we shall obtain the overall temperature gradient

$$T_1 - T_{n+1} = \frac{q}{\pi}\left(\frac{1}{2\lambda_1}\ln\frac{d_2}{d_1} + \frac{1}{2\lambda_2}\ln\frac{d_3}{d_2} + \dots + \frac{1}{2\lambda_n}\ln\frac{d_{n+1}}{d_n}\right) \qquad /79/$$

From which we can determine the amount of heat for a known temperature gradient

$$q = \frac{\pi(T_1 - T_{n+1})}{\sum_{i=1}^{i=n} \frac{1}{2\lambda_i} \ln \frac{d_{i+1}}{d_i}} \quad [\mathrm{W\,m^{-1}}] \qquad /80/$$

The expression $\frac{1}{2\lambda_i} \ln \frac{d_{i+1}}{d_i}$ $[\mathrm{mKW^{-1}}]$ is the thermal resistance of one layer.

Expression $\sum_{i=1}^{i=n} \frac{1}{2\lambda_i} \ln \frac{d_{i+1}}{d_i}$ $[\mathrm{mKW^{-1}}]$ is the thermal resistance of all the layers combined.

The temperatures at the interfaces between individual layers will be determined from equations /78/

$$T_2 = T_1 - \frac{q}{\pi} \frac{1}{2\lambda_1} \ln \frac{d_2}{d_1}$$

$$T_3 = T_1 \frac{q}{\pi} \left(\frac{1}{2\lambda_1} \ln \frac{d_2}{d_1} + \frac{1}{2\lambda_2} \ln \frac{d_3}{d_2} \right)$$

$$T_{n+1} = T_1 - \frac{q}{\pi} \left(\sum_{i=1}^{i=n} \frac{1}{2\lambda_i} \ln \frac{d_{i+1}}{d_i} \right) \qquad /81/$$

Within each layer the temperature varies logarithmically and across all the layers as shown in figure/8/ .

VIII b/ Transmission of heat by convection

Heat transmission in a fluid, from a fluid into a solid and vice versa is determined by the temperature gradient and thermal conductivity.

In the said relations, heat is transferred by both convection and thermal conduction. Convection is a mode of heat transmission in which there is macroscopic flow of the fluid, and this carries heat directly from a region of one temperature to a region of another temperature. Convection can only occur in a fluid. Convection is always accompanied with transmission of heat by conduction, the latter mode of transmission being achieved by submicroscopic motion of matter. The motion of the fluid makes the entire phenomenon of heat transmission complex, for the kind of flow depends on the mode by which the fluid is brought into motion, and also on the dimension and the shape of the solid.

Free or natural convection is a flow arising as a consequence of the difference in the densities of the hotter and cooler regions of the fluid. It can only materialize if the fluid is situated within the field of action of bulk forces, e.g. under the influence of the earth's gravity. Free convection will be considered only as due to the effect of earth gravity, with a constant gravitational acceleration g, disregarding the influence of other material forces.

Forced convection depends on a flow arising as a result of the action of external artificial forces, such as by a pump or a fan, on the fluid. A combination of the two kinds of motion may also be considered. However, the influence of natural convection is usually negligible at high velocities.

During the flow the particles move in either an orderly fashion, parallel with the channel walls, in which case we speak of streamline or laminar flow, or a disorderly fashion, in which case we are dealing with a turbulent flow. Laminar flow will change

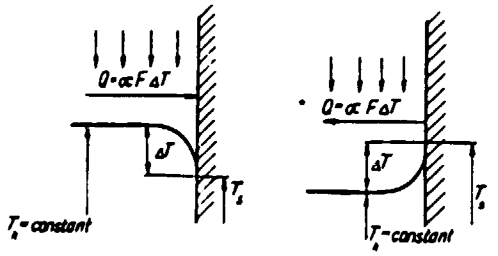

Fig.9. Heat transfer by convection /Newton's law/

into a turbulent flow when the mean flow velocity has reached critical velocity. Critical velocity differs from one fluid to another, and also varies for different geometrical conditions.

Even in turbulent flow a thin layer of fluid with a laminar flow will form next to the wall and this is called the boundary layer. The thickness of this layer diminishes as the mean flow rate increases.

The most frequent case of heat transmission by convection is a heat transfer from a fluid to the surface of a solid, or vice versa. Obviously heat always flows toward the region of lower temperature. In engineering calculations the amount of the heat transferred is often calculated from Newton's law - see Fig. 9 .

$$Q = \alpha(T_s - T_k)F \quad [W] \qquad /82/$$

where $T_s[^{\circ}C]$ — the temperature of the wall of the solid
$T_k[^{\circ}C]$ — temperature of the fluid
$F[m^2]$ — the surface area of the solid
$\alpha[Wm^{-2}K^{-1}]$ — the coefficient of heat transfer, which is the coefficient of proportionality between the heat transmitted by surface $F[m^2]$ and the temperature gradient $\Delta T = T_s - T_k\ [^{\circ}C]$.

In general, the coefficient of heat transfer has different values at different points of the surface of a solid, and consequently it can be determined exactly only for an element of surface dF

$$\alpha = \frac{dQ}{(T_s - T_k)dF} \quad [Wm^{-2}K^{-1}] \qquad /83/$$

or for a unit area

$$\alpha = \frac{q}{T_s - T_k} \quad [\mathrm{Wm^{-2}K^{-1}}] \qquad /84/$$

According to Eq. /84/ the coefficient of heat transfer α is equal to the amount of heat which is transported from the fluid through a unit area $[\mathrm{m}^2]$ into the surface of a solid-or vice versa-for a temperature difference $\Delta T = 1^{\circ}\mathrm{C}$.

Newton's law is apparently very simple, but the difficulty lies in the determination of coefficient α . This coefficient is a function of numerous quantities, such as the shape and the dimensions of the body, mode of the flow, velocity, temperature and other properties of the fluid.

We may write

$$\alpha = f(w, T_s, T_k, \lambda, c, \rho, a, \eta, \emptyset, l_1, l_2, l_3) \quad [\mathrm{Wm^{-2}K^{-1}}] \qquad /85/$$

Of the properties of the fluid the following affect the coefficient of heat transfer the most: thermal conductivity, its coefficient being $\lambda[\mathrm{Wm^{-1}K^{-1}}]$, specific heat $c[\mathrm{Jkg^{-1}K^{-1}}]$, diffusivity $a[\mathrm{m^2s^{-1}}]$, viscosity, the coefficient of which is $\eta\ [\mathrm{m^{-1}kgs^{-1}}]$. The parameters λ, c, a and ρ also have a [illegible] on the transmission of heat by conduction. By convect[illegible] viscosity η moreover, plays an important role too.

According to a rheological definition a fluid is a substance that is continuously deformed if acted upon by an arbitrarily small force.

A fluid in respect of which relation /86/ between tangential stress and rate of deformation is true, i.e.

$$\tau = \eta \frac{dv}{dn} \quad [\mathrm{N\ m^{-2}}] \qquad /86/$$

is called a Newtonian fluid. Molten glasses are also considered to be Newtonian fluids.

The dynamic viscosity η and kinematic viscosity ν are temperature-dependent physical properties peculiar to fluids /gases and liquids/. With liquids, viscosity is strongly temperature-dependent, but it is almost independent of pressure. With gases, η increases with increasing temperature and also rises with increasing pressure, but not so rapidly. With increasing temperature kinematic viscosity ν of liquids increases at about the same rate as dynamic viscosity η , since density ρ does not change substantially with temperature. Gases behave differently because density decreases rapidly with increasing temperature and kinematic viscosity thus increases rapidly.

The compressibility of liquids also affects heat transfer. It is expressed by volume compressibility, which is a unit of volumetric compliance of any substances and is determined from the change of volume with pressure, divided by the initial volume of the substance.

If the compressibility is determined at constant temperature, we are concerned with isothermal compressibility $\varkappa$, if under constant entropy, we are dealing with adiabatic compressibility. With liquids, isothermal compressibility is very small, for example for water $\varkappa_T \doteq \frac{1}{2.10^9} \left[m^2N^{-1} \right]$.

With gases, isothermal compressibility is on the contrary great, in the case for example $_T$ of air is approximately $1 \left[\frac{m^2}{1kN} \right]$. It is important to know how the gas is being compressed in the situation involved. The compressibility only needs to be considered at high velocities, above one quarter of the speed of sound. Under normal conditions, heat transmission with flowing gases may be regarded as transmission in incompressible media.

Of greater importance is the thermal expansion characterized by the coefficient of volume thermal expansivity

$$\beta = \frac{1}{V_o}\left(\frac{\Delta V}{\Delta T}\right)_{p=const} \quad \left[K^{-1}\right]\left[deg^{-1}\right] \qquad /87/$$

For liquids the value of this coefficient is low.

For an ideal gas

$$\beta = \frac{1}{273.15} = 0{,}003\ 661 \quad \left[K^{-1}\right] \qquad /88/$$

In an unevenly heated fluid,regions of different densities form, and this ultimately leads to natural convection. In free convection the condition p = const. is usually well satisfied seeing that changes in pressure are usually very small compared with the overall pressure existing in the medium.

Differential equations describing heat transfer by convection

Because heat transfer by convection depends on both thermal and hydrodynamic processes, a single differential equation will not be sufficient to define the problem; a set of equations will have to be employed. These are:

Equation of heat transfer through the boundary layer

If we are concerned with transfer of heat in one direction, e.g. y /normal to the surface of the body/ we may write the equation in the following form:

$$\alpha = -\frac{\lambda}{\vartheta_s}\left(\frac{d\vartheta}{dy}\right)_{y\to 0} \qquad /89/$$

where $\vartheta_s = T_s - T_k$ see Fig.9

$\vartheta = T - T_k$

T = temperature of the fluid in the boundary layer

λ = thermal conductivity of the fluid

Equation of continuity

The equation of continuity for compressible fluids is as follows:

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho w_x)}{\partial x} + \frac{\partial(\rho w_y)}{\partial y} + \frac{\partial(\rho w_z)}{\partial z} = 0 \qquad /90/$$

For incompressible fluids /ρ = const; $\frac{\partial \rho}{\partial t} = 0$/ the equation of continuity becomes:

$$\frac{\partial w_x}{\partial x} + \frac{\partial w_y}{\partial y} + \frac{\partial w_z}{\partial z} = 0 \qquad /91/$$

Eq./91/ may be written in the vector form:

$$\operatorname{div} \bar{w} = 0 \qquad /92/$$

ρ – density of the fluid

w_x, w_y, w_z are velocities in directions x,y,z

$\bar{w}$ – vector of velocity

Equation of heat transport through a fluid

The differential equation describing the temperature field in a fluid is deduced from the law of conservation of energy, assuming homogeneity and incompressibility of the fluid, and assuming further that there is no heat generation in the fluid itself. The equation may be written as follows:

$$\frac{\partial T}{\partial t} + w_z \frac{\partial T}{\partial x} + w_y \frac{\partial T}{\partial y} + w_z \frac{\partial T}{\partial z} = \frac{\lambda}{\rho c_p}\left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2}\right) \qquad /93/$$

The expression $\frac{\lambda}{\rho c_p}$ is thermal diffusivity a /see /48//.

The left-hand side of the equation is the total derivative of temperature T with respect to t,x,y,z and the expression in the brackets on the right-hand side of the equation is $\nabla^2 T$, /see 50/. The equation of transfer of energy /93/ can therefore be written in the form:

$$\frac{DT}{Dt} = a\nabla^2 T \qquad /94/$$

If $w_x = w_y = w_z = 0$, i.e. the fluid is not in motion, the equation will be transformed into the equation of heat transfer by conduction, and the decisive factor in the transfer will be thermal conductivity-as is the case with solids. In a steady-state heat transfer $\frac{\partial T}{\partial x} = 0$, and equation /93/ will be simplified.

From Eq./93/ it is clear that the temperature field in a fluid in motion depends on velocities w_x, w_y, w_z; the equation of heat transmission /89/ and the equation of passage of energy through a fluid /93/ have five unknowns

$$\alpha,\ T,\ w_x,\ w_y \quad \text{and} \quad w_z$$

These have yet to be supplemented by equations describing the velocity field.

Equations of motion

The basic equation for the motion of a fluid is Newton's equation of motion

$$F = ma \qquad /95/$$

where F = force,

m = mass,

a = acceleration.

An element of a fluid dx dy dz may be acted upon by body forces and surface forces. The body forces are those external forces that act on all the particles of a given volume of a fluid, such as the gravitational field of the Earth. The surface forces represent the result of the action upon the element of the fluid surrounding it. These forces act on each of the six faces of the elementary prism, generally in oblique directions. They are characterized by stresses, which include pressure and viscous stresses. The element under consideration of a fluid is then acted upon by three forces: gravity, pressure and the viscous forces.

The Navier-Stokes equations describe the flow of viscous liquids. They are valid for both laminar and turbulent flows. They can be very clearly and concisely formulated in vector form

$$\rho \frac{D\bar{w}}{Dt} = \rho\bar{g} - \nabla p + \eta\nabla^2\bar{w} \qquad /96/$$

where symbol

$$\nabla = \frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z} \qquad /97/$$

is the Hamiltonian differential operator and ∇^2 is the Laplace differential operator /see /50//.

Eq./96/ assumes the properties of the fluid to be constant and independent of temperature. This is, however, not the case. Density ρ in particular is temperature-dependent, indeed it is the differences in density that produce free convection. If the equations of motion are also to describe free convection, we must take into consideration the changes of density with temperature. A general equation expressing $\rho = f(t)$ for all fluids does not exist; therefore we shall express this dependence by the coefficient of thermal expansion β, which is practically constant for gases and also for liquids, in a limited temperature range.

For free convection, we shall consider buoyancy to be the driving force, ρ is the mean value and can be regarded as constant: dividing Eq./96/ by its value, we obtain equation of motion for the free convection caused by the differences in densities /due to differences in temperatures/ of the fluid in the vector form

$$\frac{D\bar{w}}{Dt} = \bar{g}\beta \quad - \frac{1}{\rho}\nabla p + \nu\nabla^2\bar{w} \qquad /98/$$

Transmission of heat by convection in an incompressible fluid is therefore described by the following differential equations:

for the heat transfer in the boundary layer

$$\alpha = - \frac{\lambda}{\Delta T}\left(\frac{\partial T}{\partial n}\right)_{n=0} \qquad /89/$$

for the flow of heat through a fluid

$$\frac{DT}{Dt} = a\nabla^2 T \qquad /94/$$

for the motion of a fluid

$$\frac{D\bar{w}}{Dt} = \bar{g}\beta\vartheta - \frac{1}{\rho}\nabla p + \nu\nabla^2\bar{w} \qquad /98/$$

for continuity of flow

$$\mathrm{div}\ \bar{w} = 0 . \qquad /92/$$

These differential equations describe heat transfer in general. For the solution of a specific case we must yet define a sufficient number of parameters. These are normally given by:

the geometrical data characterizing the system in which the heat transfer takes place;

the physical properties of the system;

the boundary conditions indicating the values of some parameters on the boundaries;

the initial conditions describing the state of the system at its beginning.

The latter complex of these conditions is dispensed with for steady-state phenomena.

Theory of Similarity and Modelling

The equations /89,94,98,92/ have numerous variables, and an analytical solution is possible in only a few simple cases. Solution by experiment is therefore of great importance for convective heat transfer problems. By an experiment performed under certain conditions and with certain values of parameters we can obtain numerical values of the variables being sought, and can set up equations to describe the results of the experiments.

Besides, we need to be certain that the results gained in a specific model can be transferred to an analogous process on the full-sized equipment.

Such problems are investigated by the theory of similarity. By applying the theory of similarity dimensional, physical quantities can be grouped into a smaller number of dimensionless groups. The dimensionless groups obtained in this fashion can be regarded as new variables. If introduced into the equations, the solution of such equations will be simplified, seeing that there will be fewer characteristic groups than there are separate variables. This will make it easier to determine the physical relations in the phenomena under investigation.

The theory of similarity also lays down the conditions under which it is permissible to scale up the results of laboratory observation. It provides a theoretical basis for experiments and an important tool in theoretical research. It permits us to analyse the process under observation and describe the results obtained.

To exploit the theory of similarity it is first necessary to convert the equations describing the process of heat transfer by convection into dimensionless form.

Criteria of similarity and criterial equations

The equations of heat transfer by convection will then contain certain dimensionless groups, invariants, or criteria of similarity, which have been named after scientists who contributed to advances in heat transfer and hydrodynamics.

The first of these is the Nusselt number

$$Nu = \frac{\alpha l_o}{\lambda} \qquad /99/$$

It characterizes the heat transfer on the interface separating the wall and the fluid. As a rule we are seeking the Nusselt number from the equation of heat transfer, considering that from it we determine the heat transfer coefficient α $[Wm^{-2}K^{-1}]$.

$l_o [m]$ is the characteristic dimension of the system

λ $[Wm^{-1}K^{-1}]$ is the thermal conductivity of the liquid

Another group is

$$Re = \frac{w_o l_o}{\nu} \qquad /100/$$

the Reynold's number, characterizing the ratio of the inertial and the viscous forces.

w_o $[ms^{-1}]$ is the velocity and $\nu [m^2s^{-1}]$ the kinematic viscosity of the fluid.

Another group is the Peclet number, which can be written in the following way:

$$Pe = \frac{w_o l_o}{a} = \frac{w_o l_o c_p \rho}{\lambda} = \frac{c_p w_o \vartheta}{\frac{\lambda}{l_o}\vartheta} \qquad /101/$$

where the numerator represents the heat transmitted by convection and the denominator indicates the heat transmitted by conduction.

a $[m^2 s^{-1}]$ is thermal difussivity of the fluid

c_p $[J kg^{-1} K^{-1}]$ specific heat of the fluid

ρ $[kg m^{-3}]$ density of the fluid

ϑ $[K]$ temperature difference

The dimensionless complex

$$Gr = \beta \frac{g l_o^3}{\nu^2} \vartheta_s \qquad /102/$$

is the Grashof number, which characterizes the buoyancy arising in a fluid as a result of the differences in density.

β $[K^{-1}]$ is the coefficient of volume thermal expansivity

g $[m s^{-2}]$ acceleration of gravity 9,81 ms^{-2}

ϑ_s $[K]$ mean temperature difference

As $\beta\vartheta = \frac{\rho_o - \rho}{\rho_o}$, where ρ, ρ_o are the densities of the fluid at two different points /temperatures/, we can write, as a variant of the Grashof number, the so-called Archimedes number

$$Ar = \frac{g l_o^3}{\nu^2} \frac{\rho_o - \rho}{\rho_o} \qquad /103/$$

The Archimedes number is usually used to monitor the free motion of solid particles, bubbles or drops of immiscible liquid present in another liquid. In that case ρ_o and ρ are densities of different phases.

Another dimensionless group is the Euler number

$$Eu = \frac{p}{\rho w_o^2} \qquad /104/$$

It expresses the ratio of pressure forces and the inertial forces. As we always assume an incompressible fluid with constant physical properties, we are not concerned with the absolute value of the pressure but only with a change in pressure. This is why the Euler number is usually written in the form:

$$Eu = \frac{\Delta p}{\rho w_o^2} = \frac{p-p_o}{\rho w_o^2} \qquad /105/$$

p, Δp $[Nm^{-2}]$ pressure, change in pressure

The Euler number characterizes the flow of a fluid, as a rule in a tube, caused by a pressure difference.

The dimensionless criteria of similarity, which express the ratio between the forces acting upon the fluid and its motion /the mechanical criteria of similarity/ can also be obtained from a simple comparison of forces acting upon the fluid with the inertial force.

The inertial force is

$$F = ma \qquad /95/$$

Expressingm as ρl^3 /density times volume/ and acceleration as

$$a = \frac{w}{t}\,; \qquad t = \frac{l}{w}\,; \qquad a = \frac{w^2}{l}$$

where w is the velocity and l the dimension /path/, then the inertial force is

$$F = \rho l^3 \frac{w^2}{l} = \rho w^2 l^2 \qquad /106/$$

the force due to pressure is

$$pl^2 \qquad /107/$$

that due to gravity

$$mg = \rho l^3 g \qquad /108/$$

the viscous force /shear stress times area/

$$\tau l^2 = \eta \frac{w}{l} \cdot l^2 = \eta w l \qquad /109/$$

and the surface tension force

$$\sigma l \qquad /110/$$

From a comparison of these forces with the inertial force we can obtain some of these criteria:

1. $\frac{\text{pressure}}{\text{inertia}} \dots \frac{pl^2}{\varrho w^2 l^2} = \frac{p}{\varrho w^2} \dots Eu$ (Euler N°) /111/
2. $\frac{\text{inertia}}{\text{viscosity}} \dots \frac{\varrho w^2 l^2}{\eta w l} = \frac{\varrho w l}{\eta} = \frac{wl}{\nu} \dots \mathrm{Re}$ (Reynolds N°) /112/
3. $\frac{\text{gravity}}{\text{inertia}} \dots \frac{\varrho l^3 g}{\varrho w^2 l^2} = \frac{gl}{w^2} = Fr$ (Froude N°) /113/
4. $\frac{\text{inertia}}{\text{surface tension}} \dots \frac{\varrho w^2 l^2}{\sigma l} = \frac{\varrho l w^2}{\sigma} = \mathrm{We}$ (Weber N°) /114/

In addition to the numbers already discussed we now have two others:

the Froude number, characterizing the flow of a fluid in an open channel due to gravity,

and the Weber number, characterizing the motion /flow/ of a liquid due to surface tension.

All these numbers can be raised to any powers, multiplied or divided by one another, to eliminate some quantities which are difficult to measure. In this way new criteria can be produced, for example

$$Fr\ Re^2 = \frac{gl}{w^2}\ \frac{w^2 l^2}{\nu^2} = \frac{gl^3}{\nu^2}$$

$$\frac{gl^3}{\nu^2} = Ga \qquad /115/$$

which is the Galileo number.

Multiplying this number by expression $\beta \Delta T$

$$\beta \frac{gl^3}{\nu^2} \Delta T = Gr \qquad /102/$$

we obtain the Grashof number.

Now we can write the differential equations in dimensionless form:

$$Nu = -\left(\frac{\partial\theta}{\partial Y}\right)_{Y=0} \qquad /116/$$

$$Pe\left(W_x \frac{\partial\theta}{\partial X} + W_y \frac{\partial\theta}{\partial Y} + W_z \frac{\partial\theta}{\partial Z}\right) = \nabla^2\theta \qquad /117/$$

$$Re\left(W_x \frac{\partial W_x}{\partial X} + W_y \frac{\partial W_x}{\partial Y} + W_z \frac{\partial W_x}{\partial Z}\right) = \frac{Gr}{Re}\theta - \frac{\partial}{\partial X}(Eu\ Re) + \nabla^2 W_x \qquad /118/$$

$$\frac{\partial W_x}{\partial X} + \frac{\partial W_y}{\partial Y} + \frac{\partial W_z}{\partial Z} = 0 \qquad /119/$$

where X,Y,Z ; W_x, W_y, W_z ; θ are dimensionless coordinates, velocities and temperature respectively.

These equations still have to be supplemented by similar dimensionless equations of motion for the y and z directions. The equations plus the boundary conditions then mathematically describe the transfer of heat by convection.

From the relations of individual quantities we may then write the criteria equations in a general form:

$$Nu = f_1(X,Y,Z,Pe,Re,Gr) \qquad /120/$$

$$\theta = f_2(X,Y,Z,Pe,Re,Gr) \qquad /121/$$

$$Eu = f_3(X,Y,Z,Pe,Re,Gr) \qquad /122/$$

$$W_x = f_4(X,Y,Z,Pe,Re,Gr) \qquad /123/$$

As has already been pointed out, further numbers can be obtained from the numbers already known by mathematical operations.

Thus the Peclet number

$$Pe = \frac{w_o l_o}{a}$$

can be written as

$$Pe = \frac{w_o l_o}{\nu} \frac{\nu}{a} = RePr \qquad /124/$$

where expression $\frac{\nu}{a} = Pr$ is a new dimensionless group, the Prandtl number; this criterion includes only physical properties of the fluid

$$Pr = \frac{\nu}{a} = \frac{\frac{\eta}{\rho}}{\frac{\lambda}{c_p \rho}} = \frac{\eta c_p}{\lambda} \qquad /125/$$

With liquids, Pr is temperature-dependent; in most liquids this dependence is similar to the temperature dependence of viscosity η , because the other two properties vary much less with temperature. As the temperature increases, Pr decreases.

The Prandtl number in gases is practically independent of either temperature or pressure, for a given gas it is a constant, and depends on the number of atoms of the gas.

For monoatomic gases $Pr = 0{,}67$

For diatomic gases $Pr = 0{,}72$

For triatomic gases $Pr = 0{,}8$

For tetraatomic and polyatomic gases $Pr = 1$

If we consider that $Pe = Re\,Pr$, then the equations /120-123/ may be converted into a more simple form.

For conditions in which only natural convection occurs the velocity is dependent solely on the buoyancy effects, represented by the Grashof number and the Reynolds number can be omitted. Again, when forced convection occurs the effects of natural convection are usually negligible and the Grashof number may be omitted. Thus:

for natural convection: $Nu = f(Pr,Gr)$ /126/

and for forced convection : $Nu = f(Re,Pr)$ /127/

Convection in Gases

For most gases over a wide range of temperature and pressure, the product $\frac{\mu c_p}{\lambda}$ is constant and the Prandtl number may often be omitted, making the design equations for calculation of film coefficients with gases simpler.

Forced Convection in Tubes

The results of a number of workers who have used a variety of gases such as air, carbon dioxide, and steam and of other who have used liquids such as water, acetone, kerosene, and benzene can be expressed in the general form of equation /127/ as:

$$Nu = 0{,}023\ Re^{0.8} Pr^{n} \qquad /128/$$

where n has a value of 0,4 for heating and 0,3 for cooling. In this equation all of the physical properties are taken at the mean bulk temperature of the fluid $(T_i+T_o)/2$, where T_i and T_o are the inlet and outlet temperatures. Equation /128/ is valid for Reynolds numbers greater than 10,000 and has been tested for values of the Prandtl number lying between 0,7 and 160. The difference in the value of the index for heating and cooling occurs because in the former case the film temperature will be greater than the bulk temperature and in the latter case less. Conditions in the film, particularly the viscosity of the fluid, exert an important effect on the heat transfer process.

Viscous Liquids

With very viscous liquids there will be a marked difference at any cross-section between the viscosity of the fluid adjacent to the surface and the value at the axis or at the bulk temperature of the fluid. Sieder and Tate have presented a modified equation for these conditions including a viscosity correction term:

$$Nu = 0{,}027\ Re^{0.8} Pr^{0.33} (\mu/\mu_s)^{0.14} \qquad /129/$$

where μ is the viscosity at the bulk temperature and μ_s the viscosity at the wall or surface.

Turbulent Flow of Gases

When the above equations are applied to heating or cooling of gases for which the Prandtl number usually has a value of about 0,74, substitution of $Pr = 0{,}74$ in equation /128/ gives the equation:

$$Nu = 0{,}02\ Re^{0.8} \qquad /130/$$

Special Equation for Water

Water is very frequently used as the cooling liquid, and if the variation in value of physical properties with temperature is included, then equation /128/ becomes:

$$\alpha = 1063\ (1 + 0{,}00293\ T)\ \frac{w^{0,8}}{d^{0,2}}\ [Wm^{-2}K^{-1}] \qquad /131/$$

where $T[K]$ is temperature

$d[m]$ is diameter

$w[ms^{-1}]$ is velocity

Effect of tube lenght and diameter

The effect of length to diameter ratio $/\frac{l}{d}/$ on the value of the heat transfer coefficient α is important at low Reynolds number but ceases to be significant at a Reynolds number of about 10^4.

Streamline Flow

Although heat transfer to a fluid in streamline flow takes place solely by conduction, it is convenient to consider it here so that the results can be compared with those for turbulent flow. For streamline flow through a tube the velocity distribution across a diameter is parabolic /Fig.10 /. If a liquid enters a section heated on the outside, the fluid near the wall will be at a higher temperature than that in the centre and its viscosity will be lower. The velocity of the fluid near the wall will therefore be greater in the heated section, and correspondingly less at the centre. The velocity distribution will therefore be altered, as shown. If the fluid enters a section where it is cooled, the same reasoning will show that the distribution in velocity will be altered to that shown. With a gas the conditions are reversed, because of the increase of viscosity with temperature. The heat transfer problem is therefore complex.

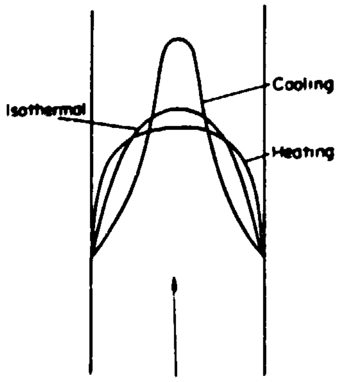

Fig.10. Effect of heat transfer on velocity distribution

For values of $(Re\ Pr\ \frac{d}{l})$ greater than 12 the following empirical equation is applicable:

$$Nu = 1,62(Re.Pr\ \frac{d}{l})^{1/3} = 1,75(G\ \frac{c_p}{\lambda l})^{1/3} \qquad /132/$$

where $G = \frac{\pi d^2}{4} . \rho w$ i.e. the mass rate of flow.

The product Re.Pr is the Peclet number - see /124/ Thus equation /132/ can be written:

$$Nu = 1,62(Pe\ \frac{d}{l})^{1/3} \qquad /133/$$

In this equation the temperature difference is taken as the arithmetic mean of the terminal values, i.e.:

$$[(T_w - T_1) + (T_w - T_2)] /2$$

where T_w is the temperature of the tube wall which is taken as constant.

If the liquid is heated almost to the wall temperature T_w /i.e. when $G.c_p/\lambda l$ is very small/ then, on equating the heat gained by the liquid to that transferred from the pipe:

$$Gc_p(T_2-T_1) = \pi dl\alpha\ \frac{T_2-T_1}{2}$$

or

$$\alpha = 2Gc_p/\pi dl \qquad /134/$$

For values of (Re Pr d/l) less than about 17, the Nusselt group becomes approximately constant at 4,1.

Viscous Liquids

Experimental values of α for viscous oils are greater than those given by equation /132/ for heating and less for cooling. This is due to the large variation of viscosity with temperature and the correction introduced for turbulent flow may also be used here, giving the equation as:

$$Nu \left(\frac{\mu_s}{\mu} \right)^{0,14} = 1,86 \left(Re\ Pr\ \frac{d}{l} \right)^{1/3} =$$

$$= 1,86 \left(Pe.\ \frac{d}{l} \right)^{1/3} = 2,01 \left(\frac{Gc_p}{\lambda l} \right)^{1/3} \qquad /135/$$

Forced Convection Outside Tubes

If a fluid passes at right angles across a single tube, the distribution of velocity around the tube will not be uniform. In the same way the rate of heat flow around a hot pipe across which air is passed is not uniform but is a maximum at the front and back and a minimum at the sides, where the rate is only some 40 per cent of the maximum. The general picture is shown in Fig. 11 but for design purposes reference is made to the average value.

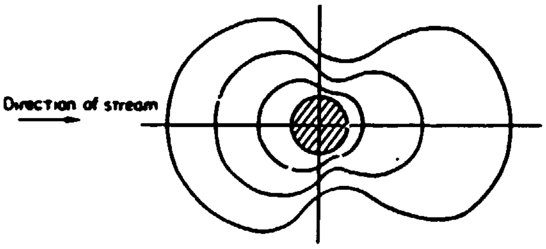

Fig.11. Distribution of film heat transfer coefficient round a cylinder with flow normal to axis for three different values of Re.

Flow Across Single Cylinders

A number of workers have studied the flow of a hot gas past a single cylinder varying from a thin wire to a tube of 150 mm diameter. They have used temperatures up to 1073 K and air velocities up to 30 m/s with Reynolds numbers /$d.w\rho/\mu$/ from 1000 to 100,000 /d_o is the cylinder diameter, or the outside tube diameter/. Their results may be expressed by the relation:

$$Nu = 0{,}26\ Re^{0{,}6} Pr^{0{,}3} \qquad /136/$$

Taking Pr as 0,74 for gases, this reduces to

$$Nu = 0{,}24\ Re^{0{,}6} \qquad /137/$$

For very low values of Re /from 0,2 to 200/ with liquids the data are better represented by the equation

$$Nu = 0{,}86\ Re^{0{,}43} Pr^{0{,}3} \qquad /138/$$

VIII c/ Heat Transfer by Radiation

A heated body emits energy in the form of electromagnetic waves. This energy is radiated in all directions and on falling on a second body is partially absorbed, partially reflected, and partially transmitted as indicated in Fig.12. The fraction of the incident radiation absorbed is known as the absorptivity a, and the fraction reflected the reflectivity of the body. The amount transmitted will therefore depend on these two properties. If the amount transmitted is negligible the material is termed opaque.

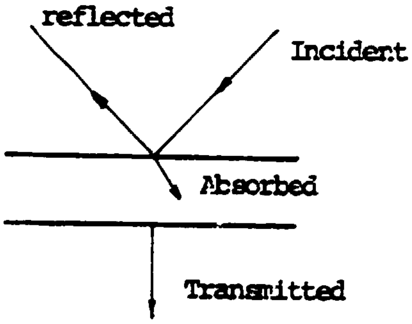

Fig.12. Reflection,absorption and transmission of radiation

Kirchhoff's Law

Suppose two bodies A and B of areas A_1 and A_2 to be in a large enclosure from which no energy is lost to the outside. Then the energy absorbed by A from the enclosure will be $A_1 a_1 I'$, where I' is the rate at which radiation is falling on A per unit area, and a_1 is the absorptivity. The energy given out by A will be $E_1 A_1$, where E_1, the emissive power, is the energy emitted per unit area per unit time. At equilibrium these quantities will be equal. In the same way the energy emitted by B will equal the energy received. Thus

$$I' A_1 a_1 = A_1 E_1 \quad \text{and} \quad I' A_2 a_2 = A_2 E_2$$

or

$$E_1/a_1 = E_2/a_2 = E/a \quad \text{for any other body} \qquad /139/$$

Thus for all bodies the ratio of the emissive power to the absorptivity will be the same. The maximum possible value for E will occur when a has its maximum value of unity. This condition applies to a black body which is defined as one which absorbs all the radiation falling on it, i.e. its absorptivity, $a_b = 1$.

Now the emissivity ε of a body is defined as the ratio of its emitting power to that of a black body; i.e. $\varepsilon = E/E_b$. Since E/a is constant for all bodies, $E/a = E_b/a_b$.

Thus

$$\varepsilon = E/E_b = a/a_b \qquad /140/$$

Then, since $a_b = 1$, the emissivity ε of any body is equal to its absorptivity a.

Energy Emitted by a Black Body

The energy emitted per unit time by a black body depends only on its temperature. This energy is given out over a range of wavelengths and the general distribution of energy from a black body at various temperatures is shown in Fig.13 . At any temperature there is a wavelength Z_m at which the maximum energy is emitted. The energy at wavelengths less than this falls off rapidly, but for wavelengths greater than Z_m the drop in energy is much less. It will be seen that the total emission increases rapidly with temperature and that the higher the temperature the smaller is the wavelength at which the maximum occurs and the more pronounced is the peak.

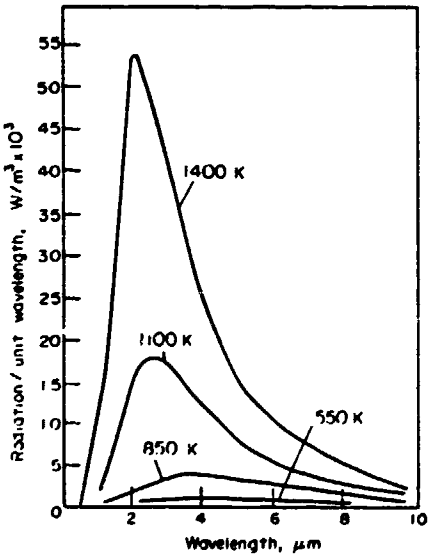

Fig.13. Emission from a black body

The wavelength of the energy radiated at temperature below 820 K is too great for it to be visible, but at higher temperatures the wavelengths correspond to those of the visible spectrum and the colour of a radiating body under these conditions is a good indication of its temperature.

The total energy emitted per unit area per unit time is given by the Stefan-Boltzmann law:

$$E = \sigma T^4 \qquad /141/$$

where T is the absolute temperature and σ is the Stefan-Boltzmann constant which has the value 5,67 x 10^{-8} $[W/m^2K^4]$. The wavelength Z_m at which the maximum energy is radiated was found by Wien to vary inversely as the absolute temperature. Taking the temperature in degrees. $TZ_m = 0,00288$, where the wavelength is in metres.

If $E_Z^{'}dZ$ is the radiation between wavelengths Z and Z+dZ, the total radiation is given by:

$$E = \int_0^\infty E_Z^{'}dZ \qquad /142/$$

It can be shown that this integral is equal to σT^4, so that:

$$E = \sigma T^4 \qquad /141/$$

Emissivity ε

The ratio of the energy emitted by a body to that emitted by a black body at the same temperature has been defined above as the emissivity. Strictly this should be taken for each wavelength, since the ratio ε will not ~~remain~~ constant over a wide range of wavelengths. A grey body is defined as one which has a constant value of ε , so that for any temperature range it radiates the same proportion of the energy radiated by a black body. Similarly it will have a constant absorptivity.

Values of ε have been measured for many materials, and it is found that for most industrial non-metallic surfaces and for non-polished metals ε may be taken as about 0,9; for highly polished surfaces such as copper or aluminium values of ε as low as 0,03 are obtained. A small cavity in a body has an effective emissivity of unity and therefore behaves as a black body.

Heat Transferred by Radiation

A body of emissivity ε at an absolute temperature T_1 emits energy $\varepsilon\sigma T_1^4$ per unit area. If the surroudings are black, they reflect back none of this radiation, but if they are at an absolute temperature T_2 they will emit radiation σT_2^4. If the body is grey it will absorb a fraction ε so that the net radiation per unit area from the grey body will be:

$$q = \varepsilon\sigma(T_1^4 - T_2^4) \qquad /143/$$

This relation will still be true where the grey body is so small that a negligible proportion of its radiation is reflected back to it from the surroudings, e.g. a body radiating to the atmosphere.

For a material that does not behave as a grey body but as a selective emitter, the absorptivity of the surface at T_1 for radiation from surroudings at T_2 will be a_{T_2}. This will not be equal to its emissivity ε_{T_1} at T_1 but to its emissivity at T_2, i.e. ε_{T_2}. Under these conditions the general equation for the net exchange of heat becomes:

$$q = \sigma(\varepsilon_{T_1}T_1^4 - \varepsilon_{T_2}T_2^4) \qquad /144/$$

Transfer Coefficient for Radiation

The net heat transfer from unit surface of a grey body at a temperature T_1 to a black enclosure at T_2 can be written as:

$$q = \alpha_r(T_1 - T_2)$$

Thus

$$\alpha_r = \frac{q}{T_1-T_2} = \frac{\sigma\varepsilon}{T_1-T_2}(T_1^4 - T_2^4) \qquad /145/$$

and α_r may be looked upon as a radiation transfer coefficient.

Equation /145/ is also applicable if the surroudings are not black, provided that the body is small and none of its radiation is reflected back to it.

The simplest case to consider is the heat exchange between two large parallel plates. In this case, all of the heat radiated by the one surface will fall on the other. In many cases, however, the second surface will intercept only part of the radiation. The fraction of the total radiation from surface 1 which is intercepted by surface 2 is referred to as the geometric or angle factor F_{12} and its value depends on the geometrical arrangement of the two surfaces. For simple configurations the geometric factors can be calculated, but for more complex arrangements they are most readily determined by experimenting with models.

For transfer between two large parallel plates, each of which has a grey surface, it will be shown that the heat transfer rate per unit area is given by:

$$q = \frac{\varepsilon_1 \cdot \varepsilon_2 \sigma}{\varepsilon_1 + \varepsilon_2 - \varepsilon_1 \varepsilon_2} \left(T_1^4 - T_2^4 \right) \qquad /145/$$

where $\varepsilon_1, \varepsilon_2$ are emissivities of the plates 1 or 2 respectively.

For long concentric cylinders or concentric spheres, the heat transfer rate per unit area of surface 1 is given by:

$$q = \frac{\varepsilon_1 \cdot \varepsilon_2 \sigma}{\varepsilon_2 + \varepsilon_1 (1 - \varepsilon_2) \frac{A_1}{A_2}} \left(T_1^4 - T_2^4 \right) \qquad /146/$$

where $\frac{A_1}{A_2}$ is the ratio of surface area of cylinder 1 /inner/ and 2 /outer/

Gas Radiation

Most of the simple monatomic and diatomic gases such as helium, hydrogen, oxygen, and nitrogen are transparent to thermal radiation, but some polyatomic gases-notably carbon dioxide, water vapour, carbon monoxide, ammonia, and hydrocarbons-absorb a considerable amount of radiation of certain frequencies. These gases, which are industrially very important, radiate appreciably in the same wave bands. In contrast with the behaviour of solids a considerable thickness of gas is required to absorb a large fraction of the radiation falling on it. Thus if I' is the intensity of the incident radiation, the intensity I after the radiation has passed through a layer of thickness x is given by:

$$I = I' e^{-m' x} \qquad /147/$$

where m' will,in general, vary with the wavelength as is approximately proportional to the partial pressure of the gas for any one wavelength, i.e. to the number of molecules per unit volume. The absorption will then be a function of the product $p_g l$, where p_g is the partial pressure of the gas and l is the equivalent thickness of the gas stream. The absorptivity of a gas is conveniently plotted against temperature for a constant value of $p_g l$. The thickness l is assumed the same in all directions but this will only be true for the case of a hemisphere where the gas is radiating to the mid-point of its base. It has been found that for a wide range of conditions l may be taken as 3,4 times the gas volume divided by the area of the retaining walls. A few values on this basis are given in Table

Table VIII. Equivalent dimensions for hemispherical radiation

Shape	Characteristic dimension L	Equivalent dimension for hemispherical radiation
Sphere	Diameter	$0{\cdot}57L$
Infinite cylinder radiating to walls	Diameter	$0{\cdot}86L$
Space between infinite parallel planes	Distance apart	$1{\cdot}70L$
Space outside bank of tubes with centres on equilateral triangle; clearance = diameter of tube	Clearance	$2{\cdot}89L$
Ditto, with tube centres on square pitch; tube diameter = clearance	Clearance	$3{\cdot}49L$

Curves showing the emissivity of water vapour at a total pressure of one atmosphere, are in Fig. 14. The net radiant heat exchange between a gas at T_1 and unit area of enclosure at T_2 acting as a black body will be:

$$q = \sigma(\varepsilon_g . T_1^4 - a_g T_2^4) \qquad /148/$$

where ε_g and a_g are the emissivity and absorptivity of the gas.

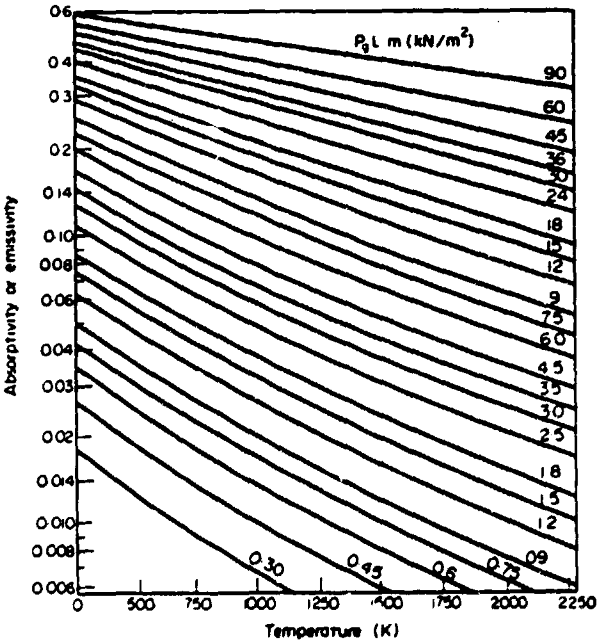

Fig.14. Absorptivity and emissivity of water vapour

If the enclosure acts as a non-black surface some of the radiation falling on it is reflected back; of this, part is absorbed by the gas and part by the surface. For these general conditions it is usually sufficiently accurate to take the emissivity of the enclosure as ε', where $\varepsilon' = (\varepsilon_s + 1)/2$. This is permissible because ε_s, the emissivity of the surface, will probably lie between 0,7 and 1. The radiation exchange will then be:

$$q = \varepsilon' \sigma (\varepsilon_g T_1^4 - a_g T_2^4) \qquad /149/$$

References

R. Griffiths, C. Radford: Calculations in Ceramics, Maclaren and Sons Ltd. London, England 1965

V. Lach: Keramická příručka /Ceramic Handbook/. SNTL, Publishers of technical literature Prague 1958

J. Hlaváč: The technology of glass and ceramics, Elsevier, Amsterdam 1983

J.M.Coulson, J.F.Richardson: Chemical Engineering, Vol.I. Pergamon Press, Oxford, N.York

J. Staněk: Electric Melting of Glass, Elsevier, Amsterdam 1977