As a result of these experiments, it appears that a number of bodies, quite complex in character, may be had, which seems to show the existence of a series of compounds of lanthanum which may be termed meta-lanthanates or poly-meta-lanthanates. At the same time it is quite evident from this and other work which immediately follows, that the methods are not suitable as a means of separation of these rare earths, and really little value can be attached to the above.

A per-lanthanate, or hydrated peroxide, $La_2O_5.xH_2O$, was obtained by fusion with sodium peroxide. Such a body has already been reported by Melikoff and Pissarjewsky.[1]

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THE THERMAL EFFICIENCY OF A ROTARY CEMENT KILN.[2]

BY JOSEPH W. RICHARDS.

THE following tests and results were obtained on a rotary cement burner, 60 feet long by 6 feet external diameter, fired by pulverized bituminous slack coal, at the plant of the Dexter Cement Company, at Nazareth, Pa.[3]

The ground cement mixture has the following composition:

	Per cent.
Silica	13.38
Aluminum oxide } Ferric oxide	6.04
Calcium oxide	41.96
Magnesium oxide	1.53
Carbon dioxide	34.65
Moisture	0.43

The burnt cement clinker contains:

	Per cent.
Silica	21.27
Aluminum oxide	6.42
Ferric oxide	3.18
Calcium oxide	66.70
Magnesium oxide	2.43

The bituminous slack coal from Fairmount, W. Va., analyses:

Per cent.

Moisture............................ 0.60
Volatile combustible matter........ 38.10
Fixed carbon 53.24
Ash 8.06

The following ultimate composition of the coal was assumed from average analyses of coal from that region of similar proximate composition:

Per cent.

Carbon 73.60
Hydrogen 5.30
Nitrogen 1.70
Sulphur 0.75
Oxygen 10.00
Moisture........................... 0.60
Ash 8.05

The kiln turns out an average of 3635 pounds of clinkered cement per hour from 5980 pounds of mixture fed to it, producing 200 pounds of flue dust, equal to 3.35 per cent. of the weight of mixture charged.

The coal used averages 110 pounds per barrel (of 380 pounds) of cement produced, a quantity practically equal to 50 kilograms per barrel, or 2 barrels per 100 kilograms of coal. On account of the convenience of making calculations in the metric system, and of the coincidence noted above, the calculations will all be made on the basis of 100 kilograms of coal used, or per 2 barrels of cement made.

<center>EXPERIMENTAL DATA.</center>

Temperature of the clinker falling out of the lower end of the kiln, measured by the Le Chatelier pyrometer, 1200° C.= 2192° F.

Temperature of the waste gases in the chimney, 4 feet from the upper end of the kiln, 820° C. = 1508° F.

Sensible heat in the clinker leaving the kiln at 1200° C., measured by a calorimeter: kilogram calories per kilo 290; British thermal units per pound, 522.

Composition of the waste gases in the stack:

Per cent.

Carbon dioxide 10.2
Oxygen 11.8
Carbon monoxide 0.2
Sulphur dioxide ⎫
Water   ⎬ ...... not determined
Nitrogen   ⎭

Temperature of the atmosphere, 20° C.; saturated with moisture.

The object of the tests and calculations is to make a balance sheet of the heat generated within the kiln, and of its distribution, to find out the temperature of the hot gases which communicate their heat to the clinker, and the proportion of air used in excess of that theoretically needed for perfect combustion.

The items of the heat balance sheet are:

Heat Developed.

(1) Theoretical heating power of the fuel.

(2) The chemical heat of combination of the ingredients forming the clinker.

Heat Distribution.

(1) Heat in hot clinker.

(2) Heat in chimney gases as sensible heat.

(3) Heat in flue dust as sensible heat.

(4) Heat lost by imperfect combustion.

(5) Heat required to expel moisture from charge.

(6) Heat required to expel carbonic acid from carbonates.

(7) Heat lost by radiation and conduction (by difference).

Heat Developed.

(1) *Theoretical Heating Power of the Fuel.*—This was calculated from the proximate composition by the formula of F. Haas, published in Vol. II of the Report of the Geological Survey of West Virginia.[1] This calculation should be within 1 per cent. of the actual calorimetric value of the coal and gives:

Calorific power of 1 kilogram in kilogram calories, 7,900; calorific power of 1 pound in British thermal units, 14,225.

(2) *Heat of Formation of the Clinker.*—There was formed, per 100 kilos of coal burnt, 2 barrels, equals 760 pounds or 345 kilos of clinker. This contains, from its analysis,

	Kilos.
Calcium oxide	230.
Magnesium oxide	8.4
Ferric oxide	11.0

The assumption is now made that these occur as carbonates in the charge, and that the heats of combination with silica or alumina,

[1] *Mines and Minerals*, September, 1903.

to form silicates or aluminates, are 591 calories per kilo of lime and 827 calories per kilo of magnesia, as derived from the heats of combination given by Berthelot, in his "Thermochimie," Vol. II.

The heat of formation of the clinker, when heated up to the temperature at which combination takes place, is therefore

Calories.

For the lime .... $230 \times 591 = 135,930$
For the magnesia............... $8.4 \times 827 = 6,889$

Total.............. $142,819$

Heat Distribution.

(1) *Heat in the Hot Clinker.*—A calorimeter containing 790 grams of water, was held under the outlet, and 95 grams of hot clinker caught in it. The weight of clinker used was determined after the experiment by filtering out the clinker, drying, heating to redness and weighing. The clinker at 1200° C. heated the water from 20.5° to 54.5°, a rise of 34°, thus giving out, in falling to 54.5°, $(790 \times 34) \div 95 = 283$ gram-calories per gram of clinker. As the prevailing outside temperature, used as a base, was 20° C., the clinker would have given out more than 283 calories had it fallen to 20°. Assuming its specific heat in this range as 0.20, the correction is $0.20 \times 35 = 7$ calories, and the total heat in the clinker above 20° C. is $283 + 7 = 290$ calories.

The total heat in the hot clinker made is therefore $290 \times 345 = 100,050$ calories.

It may be remarked that the mean specific heat of the clinker between 20° C. and 1200° C. is $290 \div 1180 = 0.246$.

(2) *Heat in Chimney Gases as Sensible Heat.*—Analysis shows the gases to contain in 1 cubic meter, 0.102 cubic meter of carbon dioxide and 0.002 cubic meter of carbon monoxide, or, together 0.104 cubic meter of the two gases, which each contain 0.54 kilo of carbon per cubic meter. Therefore we have in gas measured cold: carbon in 1 cubic meter of chimney gas — $0.102 \times 0.54 = 0.05616$ kilo.

The carbon going into the gases per 100 kilos of coal burnt is as follows:

Kilos

Carbon in 100 kilos of coal, by analysis................. 73.6
Carbon expelled from the charge as CO_2:
    From calcium carbonate...... $230 \times {}^{12}/_{56} = 49.3$
    From magnesium carbonate .. $8.4 \times {}^{12}/_{40} = 2.5$
                                          51.8

Total going into the gases 125.4

Therefore, volume of gas per 100 kilos of coal burnt, is 125.4 ÷ 0.05616 = 2233 cubic meters of gas, as analyzed, calculated dry. Of this gas, 10.2 per cent. is carbon dioxide, 0.2 per cent. carbon monoxide, 11.8 per cent. free oxygen, and, by calculation, only 0.025 per cent. of sulphur dioxide, leaving 77.8 per cent. of nitrogen = 1737 cubic meters of nitrogen in the gases. Sulphur dioxide in the gas, from 100 kilos of coal = 0.75 × 2/2.88 = 0.5 cubic meter. Water in gas, per 100 kilos of coal burnt:

			Cubic meters.
In charge	568 kilos × 0.0043 = 2.44 kilos =	3.0
In coal	100 kilos × 0.0060 = 0.60 kilos =	0.7
From hydrogen in coal	100 × 0.0530 × 9 = 47.70 kilos =	58.9
From water in air	$17.35 \times {}^{100}/_{19.2} \times {}^{27}/_{135} =$	65.4
	Total	128.0

Total gases per 100 kilos of coal burnt:

	Cubic meters.
Nitrogen	1737
Oxygen	263
Carbon monoxide	4
Carbon dioxide	228
Water vapor	128

The mean specific heat of these gases is, from the experiments of Mallard and Le Chatelier, per cubic meter (at standard conditions):

Nitrogen, oxygen, carbon monoxide .... $0.303 + 0.000027\ t$
Carbon dioxide .... $0.37 + 0.00027\ t$
Water .... $0.34 - 0.00015\ t$

The mean specific heats of these gases, between 20° C. and 820° C., can therefore be calculated, and these, multiplied into the volumes of gases escaping, measured at standard conditions, gives the sensible heat going up the chimney, per degree of temperature of the gases:

	Cubic meters.	
Nitrogen	1737	
Oxygen	263	
Carbon monoxide	4	
	2004 × 0.325 =	651
Carbon dioxide	228 × 0.591 =	135
Water	128 × 0.463 =	59

$$845 \times (820 - 20) = 676{,}000 \text{ calories.}$$

Of this total, a very large part is carried by the air used in ex-

cess of that needed for perfect combustion. Practically perfect combustion can be attained with a much smaller excess of air than is used above. Of the 263 cubic meters of oxygen, 2 would be needed to burn the carbon monoxide completely, leaving 261 cubic meters used in excess. This carried in with it 988 cubic meters of nitrogen and 39.5 cubic meters of moisture, and therefore carries out the following amounts of heat.

Cubic meters.

Nitrogen 261
Oxygen 988
                      ‾‾‾‾
                      1249   × 0.325 = 406
Water..... .... 39.5 × 0.463 = 14
                               ‾‾‾‾
                      420 × (820 — 20) = 336,000 calories.

Leaving, as carried out by the normal gases produced, if no excess of air were used, 676,000 — 336,000 = 340,000 calories.

It is interesting to note that the ratio of air actually admitted, to air actually used, is as the nitrogen in the gases (subtracting that in the coal) to the nitrogen in the proper products of combustion, *viz.*, as 1735 to (1735 — 988), or as 2.32 to 1.

(3) *Heat in Flue Dust.*—There are 12 kilos of dust carried out per 100 kilos of fuel burnt, carrying out, therefore,

$$12 \times 0.22 \times (820° - 20°) = 2,112 \text{ calories.}$$

(4) *Heat Lost by Imperfect Combustion.*—There are 4 cubic meters of carbon monoxide escaping unburnt, causing a loss by imperfect combustion of

$$4 \times 3062 = 12,248 \text{ calories.}$$

(5) *Heat Absorbed in Evaporating the Water of the Charge.*—The charge contains 2.44 kilos of water per 100 of fuel burnt. We have already allowed for the sensible heat which this carries out, and need here allow only for the heat required to convert it into vapor, which is 593 calories per kilogram at 20° C.

$$2.44 \times 593 = 1,446 \text{ calories.}$$

(6) *Heat required to expel carbon dioxide from carbonates.*—

Kilos.

Carbon dioxide from calcium carbonate..... = $49.3 \times {}^{44}/_{12}$ = 180.8
Carbon dioxide from magnesium carbonate.. = $2.5 \times {}^{44}/_{12}$ =   9.2

To expel 1 kilo of carbon dioxide from calcium carbonate requires 990 calories, and from magnesium carbonate 407 calories, according to Berthelot's "Thermochimie."

Calories.
$$180.8 \times 990 = 17,896$$
$$9.2 \times 407 = \underline{3,732}$$

Total, 21,628

(7) *Heat Lost by Radiation and Conduction.*—This might be experimentally determined, but only approximately. It is best found by the difference between the heat generated and the sum of all the other items of heat distribution.

<div align="center">RECAPITULATION.</div>

Heat Generated.—

Calories.
(1) Theoretical heating power of the fuel................. 790,000
(2) Heat of combination of the ingredients forming clinker 142,819

Total.............. 932,819

Heat Distribution.—

	Calories.	Percentage of whole.
(1) Heat in the hot clinker.................	100,050 =	10.7
(2) Heat in the chimney gases :		
(*a*) In the excess air admitted..... 336,000	= 36.0	
(*b*) In the necessary products..... 340,000	= 36.1	
	676,000 =	72.1
(3) Heat in flue dust.........................	2,112 =	0.2
(4) Loss by imperfect combustion	12,248 =	1.3
(5) Evaporation of water of charge	1,446 =	0.2
(6) Expulsion of carbon dioxide from carbonates	21,628 =	2.3
(7) Loss by radiation and conduction.........	119,335 =	12.8
	932,819	

<div align="center">REMARKS.</div>

The interesting facts brought out by the above analysis are the following :

(*a*) The combination of the ingredients of the cinder evolves a large quantity of heat, equal to 18 per cent. of the heat developed by the combustion of the coal. This quantity is surprisingly great, but is a reality from the chemical standpoint ; and, moreover, if it were left out of consideration there would be a deficit on the distribution side without making any allowance for loss by radiation and conduction. The heat of chemical combination is, therefore, an important item in the development of heat which cannot be neglected.

(*b*) The heat in the clinker represents only a trifle over one-

tenth of the heat developed in the kiln.   This is a very low proportion for an industrial operation, and leaves large room for improvement and economies where fuel is dear.

(c) The great amount of heat carried out by the products of combustion and excess of air, amounting to nearly three-quarters of the total heat developed in the kiln, and over 85 per cent. of the calorific power of the fuel.   This points to the greatest heat losses in the kiln, for if the temperature of the gases were reduced one-half by the use of a kiln approximately twice as long, the heat saved would amount to some 40 per cent. of the calorific power of the fuel.   If the amount of air admitted were reduced to 10 per cent. excess instead of 132 per cent. excess as it now stands, the heat carried out by the hot gases would be reduced in that case also by an amount equal to 40 per cent. of the calorific power of the fuel.   If both economies were practiced at once, the saving might amount to over 60 per cent. of the amount of fuel used.

(d) The loss by radiation and conduction is small, but might be considerably reduced at the lower end of the kiln by an asbestos lagging.   This might not be practicable, however, if it resulted in the iron shell becoming too hot and being burnt out.

(e) The amount of air admitted to the kiln is found by calculation to be 132 per cent. in excess of that theoretically required for the perfect combustion of the fuel.

TEMPERATURE OF THE FLAME.

It is interesting to calculate what the maximum temperature of the mixed gases of combustion and excess of air can be in the kiln. The available heat of combustion of the fuel is 790,000 calories, and this is taken up by the products of combustion and the excess of air, *viz*:

Cubic meters.

Nitrogen .... 1737 ⎤
Oxygen .... 263 ⎬ 2004 cubic meters.
Carbon monoxide....... 4 ⎦
Carbon dioxide 136
Water vapor............ 128

The maximum temperature of the gases in the kiln is the temperature to which the 790,000 calories will heat these volumes of gas.   Using the formulas for the specific heats of these gases, as previously used in this paper, the expression for the temperature becomes

$$t - 20° = \frac{790,000}{\left\{2004 \times [0.303 + 0.000027(t+20)]\right\} + \left\{136 \times [0.37 + 0.00027(t+20)]\right\} + \left\{128 \times [0.34 + 0.00015(t+20)]\right\}}$$

from which $t = 1000°$.

An extremely interesting fact is here brought out; *viz.*, that the clinker, leaving the kiln at 1200°, is hotter than the mixture of gases in the kiln. It is its heat of combination which causes this, and which accounts for the anomaly. In fact, the heat of combination probably heats the clinker even hotter than 1200°, in the interior of the kiln. In other words, when the ingredients of the cement are brought to their combination point by the gases in the kiln, a point practically about 1000° C., they ignite and combine, like a pile of anthracite coal igniting when heated to redness, and become, by their own heat of chemical combination, much hotter than the temperature to which the gases have heated them.

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DETERMINATIONS OF ALKALIES IN THE PRESENCE OF BORATES.

BY K. JACOBI.

DISSOLVE 2 grams of the substance to be determined in hydrochloric acid, evaporate to dryness and bake for an hour. After cooling, add dilute hydrochloric acid, boil and filter off the silica. Precipitate iron oxide and alumina by slight excess of ammonia and the calcium oxide by ammonium oxalate. Precipitate the magnesia by ammonium phosphate and remove the excess of phosphoric acid by adding pure ferric chloride to the solution and precipitating the ferric phosphate with ammonia, which, of course, will also remove the excess of iron. Generally—at least as regards deposits in this country—when borates occur in large amounts, there are no bases other than those mentioned. Should any sulphates be present, the sulphuric acid ought to be determined separately and taken into account when the final calculation is made. Now evaporate the solution to dryness with 40-50 cc. of strong nitric acid and repeat a second time with 20 cc. to insure complete removal of ammonium salts. Take up in hydrochloric acid (strong), evaporate to dryness and repeat. After the second evaporation, add water, boil, filter into a tared platinum dish and