is then allowed to cool to about 80°, a solution of 3½ to 4 grams of glacial phosphoric acid in water is then added, and the mixture kept at this temperature for a few minutes. The mixture is then cooled to room temperature, filled up to the mark with water, thoroughly mixed by shaking and filtered.

It may be assumed that the volume of the precipitate is equal to that obtained by precipitation with mercury solution. Enough potassium hydroxide is then added to almost but not quite neutralize the free acid, and sufficient water is added to make up for the volume of the solids precipitated by the phosphoric acid. The mixture is then filtered and the filtrate is measured in portions of 100 cc. each, into 200 cc. flasks. A solution containing about twenty mgms. of potassium fluoride, and a half cake of Fleischman's compressed yeast, are then added to each flask and the mixture is then allowed to stand for ten days in a room whose temperature is 25° to 30°. The flasks are filled up to the mark, and the milk sugar is determined either by copper reduction or by means of the polariscope.

Invert Sugar.—The weight of cuprous oxide reduced by milk sugar and invert sugar, less the equivalent of the milk sugar found after fermentation, is due to invert sugar.

CHEMICAL CONSIDERATIONS ON THE POTTERY INDUSTRIES OF THE UNITED STATES.

BY KARL LANGENBECK.

Received November 27, 1893.

PART II.

Rockingham and Yellow Ware.—A higher grade of ware, than that last treated is "Rockingham and Yellow Ware;" though belonging to the same ceramic category, namely, "Faience," in that it also consists of a porous body covered with a transparent lead glaze.

It differs from "red ware" in color, and in having a body requiring a higher temperature for its proper burning, so that the glaze is not applied to the freshly formed pieces in their "clay state," but to the once baked or "biscuit" pieces, and is then finished in a second or "glost" fire softer than the first.

The clays used for "yellow ware" belong to the class commercially known as second-class fire clays: the same from which common fire brick and such terra-cotta articles as stove and flue linings, chimney tops, garden vases, etc., are made. They are generally the common "buff" or "blue" clays of the coal measures and are widely distributed in all our carboniferous exposures.

A typical clay of this character has the following composition:

TOTAL ANALYSIS.

	Per cent.	Insol. in H_2SO_4 Per cent.
Silica	60.50	22.33
Alumina	25.53	0.53
Ferric Oxide	1.66	0.26
Titanic Oxide	0.54	....
Manganous Oxide	0.33	....
Lime	0.38	0.26
Magnesia	1.19	0.07
Alkalies	1.76	0.37
Combined Water	7.98	....
	99.87	23.82

RATIONAL ANALYSIS.

	Per cent.
Clay Substance	76.05
Quartz	19.54
Feldspathic detritus	4.28
	99.87

CHEMICAL COMPOSITION OF THE "CLAY SUBSTANCE."

	Per cent.
Silica	50.19
Alumina	32.87
Ferric Oxide	1.84
Titanic Oxide	0.71
Manganous Oxide	0.43
Lime	0.16
Magnesia	1.47
Alkalies	1.82
Combined Water	10.50

The yellow ware potter is better equipped in machinery than the red ware potter, and does not, like the latter, prepare his clay by merely soaking it with water and then tread and knead it to a plastic mass of the proper consistence; but subjects the clay to a regular washing process. Hence the presence of a certain amount of coarse sand and nodules and particles of iron pyrites, very commonly found in all such clays, do not spoil them for his work, as they are removed by the necessary and customary process of manufacture.

This consists in "slipping" the clay in a vat with mechanical stirrers, known as a "blunger," sifting the "slip" through a sixty-mesh wire sieve or a No. 8 silk lawn stretched over a vibrating frame, from which the coarser sandy impurities are thrown, and condensing the "slip" to plastic clay by evaporation or by a filter press.

From this process, it will be realized that the clay must be in such a condition of physical aggregation as to be easily disintegrated or "slipped" by mere stirring in water. A hard clay readily reduced by the elements in "weathering" to such a condition, will also answer the purpose; but the double shoveling involved in transferring clay from the bank to a weathering flat, and from thence, after six months or a year's exposure to the elements, to the factory, is a trouble the potter avoids if he can.

There is a class of clays, which from their composition are admirably adapted for yellow ware, but have remained completely barred from this use because of their physical character. These are the "flint clays" of which the following analysis is typical:—

TOTAL ANALYSIS.

	Per cent.	Insol. in H_2SO_4. Per cent.
Silica	55.04	16.96
Alumina	29.85	0.11
Ferric Oxide	1.76	....
Lime	0.79	0.12
Magnesia	0.57	0.17
Alkalies	1.83	0.58
Combined Water	10.95	....
	100.79	17.94

RATIONAL ANALYSIS.

	Per cent.
"Clay Substance"	82.85
Quartz	16.58
Feldspathic detritus	1.35
	100.78

PERCENTAGE COMPOSITION OF THE "CLAY SUBSTANCE."

	Per cent.
Silica	45.97
Alumina	35.90
Ferric Oxide	2.12
Lime	0.81
Magnesia	0.48
Alkalies	1.51
Combined Water	13.22
	100.00

This clay occurs in rocky masses having a conchoidal fracture, the splinters of which are so hard and sharp, that a flying piece, struck off with the pick, will cut the hand or face. It eagerly absorbs water and with a crackling noise, though without noticeable evolution of heat, falls to pieces, yielding a mass of shell-like splinters, though a year's exposure to the weather, while reducing it to a fine sand, fails to produce a workable clay. Simple grinding in water and thickening the resulting "slip," by any convenient method, produces a highly plastic mass, that is readily formed into ware, burns to a bright yellow color, and bears the customary yellow ware glazes with less danger of "crazing" than the before-mentioned and commonly used clay. This latter fact is to be accounted for by the extreme fineness of the contained quartz, more than compensating for the reduced quantity of the same.

The expense of wet grinding a "flint clay" would not be excessive, but the introduction of machinery for the purpose, in so conservative a craft as the one under consideration, would be met with almost stolid resistance.

The first or "biscuit" fire of yellow ware, for hardening the clay pieces, must reach "good biscuit heat," that is a temperature sufficient to bake the clay so hard that it can no longer be cut with a knife, but that the steel leaves a lead-pencil-like mark on the surface. At the same time, the shard must still be porous and adhere when touched to the tongue.

The temperature of the "biscuit" fire will necessarily, of course, vary with the chemical and physical character of the clay used. The potter determines it empirically by testing-trials of the clay drawn from the kiln, with his knife and tongue.

It is very important that the chemist determine at what heat the clay he is examining attain a "good biscuit" condition, in order that the potter may know whether he can introduce ware made of it into his biscuit kiln along with his old ware. As a kiln of ware represents considerable capital exposed to a risky operation, potters naturally are absolutely opposed to the adoption of new clays requiring different conditions of fire from those already adopted by them; these must dovetail easily at least into their kiln conditions, by requiring the same heat.

For the purpose of such heat tests the most accurate and convenient appliance is the Seger pyrometric cone. The cones are easily used, not influenced by momentary flashes of unequal heats, but melt down at the corresponding average temperature of a certain period of time (which is what determines the character and hardness of the baked product); they accord perfectly with others of the same number, are cheap and if not easily obtained can even be made by the operator himself.

Yellow ware clays reach the required hardness at temperatures varying from the melting points of cones V, to VII, or even VIII.[1]

			Per cent.
V.	$\left.\begin{matrix}0.3\ K_2O\\ 0.7\ CaO\end{matrix}\right\}0.5\ Al_2O_3\ 5.\ SiO_2$	Orthoclase	83.55
		Marble dust	35.00
		Quartz	84.00
		Kaolinite	25.90
VI.	$\left.\begin{matrix}0.3\ K_2O\\ 0.7\ CaO\end{matrix}\right\}0.6\ Al_2O_3\ 6.\ SiO_2$	Orthoclase	83.55
		Marble dust	35.00
		Quartz	108.00
		Kaolinite	38.85
VII.	$\left.\begin{matrix}0.3\ K_2O\\ 0.7\ CaO\end{matrix}\right\}0.7\ Al_2O_3\ 7.\ SiO_2$	Orthoclase	83.55
		Marble dust	35.00
		Quartz	132.00
		Kaolinite	51.80
VIII.	$\left.\begin{matrix}0.3\ K_2O\\ 0.7\ CaO\end{matrix}\right\}0.8\ Al_2O_3\ 8.\ SiO_2$	Orthoclase	83.55
		Marble dust	35.00
		Quartz	156.00
		Kaolinite	64.75

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[1] *Thonindustrie Zeitung*, 1886, p. 169.

For "yellow ware" as for "red ware," it is customary to employ a "raw" glaze, that is, one containing no soluble constituents which have first to be rendered insoluble by fritting to a glass.

The customary type of glaze has a formula resembling one of the following: $1.0\ PbO\ 0.2\ Al_2O_3\ 2.0\ SiO_2$, which may be made by grinding together:

129.7	White Lead
25.9	China Clay
48.0	Flint

$$\begin{array}{l} \left.\begin{array}{l} 0.8\ PbO \\ 0.2\ K_2O \end{array}\right\} 0.2\ Al_2O_3\ 2.\ SiO_2 \text{ from} \\ \overline{1.0} \end{array}$$

103.8	White Lead
55.7	Feldspar
24.0	Quartz

$$\begin{array}{l} \left.\begin{array}{l} 0.8\ PbO \\ 0.1\ CaO \\ 0.1\ K_2O \end{array}\right\} 0.2\ Al_2O_3\ 2.\ SiO_2 \\ \overline{1.0} \end{array}$$

obtained by grinding together:

103.8	White Lead
27.9	Feldspar
13.0	China Clay
5.0	Carbonate of Lime
36.0	Quartz

The acidity of the glaze generally varies from 1.8 to 2.2 SiO_2, depending upon the amount of quartz contained in the clay upon which it is expected to stand. The alumina will similarly vary from 0.16 to 0.2 and over according to the stiffness of the glaze required and the conditions of firing, causing a liability to devitrification, or most likely as chance has thrown a fairly satisfactory formula into the potter's hands.

The temperature at which the glazes run bright lies about at a point at which an alloy composed of

50 per cent. Silver
50 " " Gold

will melt, though depending upon the composition of the glaze, and the length of fire, the melting point of the alloy.

75 per cent. Gold
25 " " Silver

may have to be reached.

"Rockingham ware" differs from "yellow ware" only in that it is covered with a brown manganiferous glaze, applied either by spattering the piece, previously dipped in the clear glaze, with the same, thus producing a mottled effect by the melting of the glazes into each other, or by directly dipping the biscuit piece into the "Rockingham" glaze alone, whereby the fired piece obtains a uniform red-brown finish.

Common forms of Rockingham glazes are the following:

$$\left.\begin{array}{l}0.85\ \mathrm{PbO}\\ 0.15\ \mathrm{MnO}\end{array}\right\}0.18\ \mathrm{Al_2O_3}\ 1.8\ \mathrm{SiO_2}$$

$$\overline{1.00}$$

made by grinding together:

110.0 White Lead
6.5 Black Oxide of Manganese
23.3 China Clay
43.2 Flint

also,

$$\left.\begin{array}{l}0.9\ \mathrm{PbO}\\ 0.1\ \mathrm{MnO}\end{array}\right\}\left.\begin{array}{l}0.15\ \mathrm{Al_2O_3}\\ 0.05\ \mathrm{Fe_2O_3}\end{array}\right\}2.\ \mathrm{SiO_2}$$

$$\overline{1.0}$$

similarly prepared with a ferruginous clay, the formula of which any chemist will be able to figure out from the equivalent proportions given.

As in the case of "red ware" the prevailing fire of both the biscuit and glost kilns should be oxidizing.

The ware manufactured in this industry embraces such kitchen and other domestic utensils as bowls, bakers, nappies, chambers. tea and coffee pots, pitchers, etc.

In examining a clay for its possible use in this manufacture it is important to determine whether it can readily be disintegrated by stirring or boiling in water, or whether repeated soaking and drying or freezing and thawing it bring it to such a state.

A "slip" of the clay should be run through a sixty mesh wire sieve and the amount and character of the remaining sand given.

If the latter is at all appreciable the sample for analysis should not be taken from the crude clay, as this would, of course, give an entirely false idea of the constituents ultimately entering the potter's "body," but the sample should be taken from the thickened and dried "slip" which has passed the sixty mesh sieve. Such a "slip" is readily thickened by pouring it on a thick, clean, and dry slab of plaster paris, which readily absorbs the water and from which the plastic clay is readily peeled without danger of contamination with plaster.

A part of the now plastic clay is dried for preparation of the sample for a "rational" analysis, in the customary manner. The bulk of the washed product is formed into cakes and rings for the burning. The latter are made for the purpose of watching the progress made by the clay in the fire, and determining when the baking is finished. These rings should be of such size, as to be readily withdrawn from the muffle with a stout iron wire, through the spy-hole in the door of the same.

When the clay pieces are bone-dry, they are placed in the muffle on a thick bed of clean quartz sand or a thick fire-clay tile strewn with the same.

The rings should be so placed as to be easily reached through the spy-hole in the door brick and parallel with them the Seger cones V, VI, VII, and VIII, should be set upright on a piece of tiling or flat cake of baked or raw clay, to which they had best be stuck with a little "slip." The door brick is then luted in place with a wad of soft clay, and the firing begun gradually, raising the heat at an increasing rate.

Should there be difficulty in seeing the pyroscopes when the muffle has reached bright redness, on removing the plug from the spy-hole, the careful introduction of a thick iron wire in their neighborhood, will momentarily so far reduce their temperature as to make them clearly discernible against the bright walls of the muffle.

When cone V crooks over, the first clay ring should be drawn from the muffle with a wire and when cool, tested with the knife for hardness, if insufficient the firing is continued until cone V has melted down completely, when the second ring is drawn. The next trial is drawn at the crooking of cone VI, and so on until a heat is reached at which the clay trial ring is sufficiently hard to resist cutting with a knife, without having lost all porosity, adhering when touched to the tongue.

When this heat is reached the firing is discontinued and the furnace allowed to cool.

The fired pieces of clay removed from the cold muffle are covered on one side with one of the described glazes, of which I would recommend the first, which is easily made and fired as a convenient empirical standard, against which to test the coefficient of expansion of the baked clay.

The pieces are then baked a second time to melt the glaze upon them, the heat reached being that of the melting point of the alloy,

50 per cent. Silver,
50 " " Gold.

It is also very convenient to use the small baked trial rings partly covered with the glaze as trials for this fire, the firing being discontinued when the glaze on one of these rings drawn from the muffle has run bright.

The color of the clay under the clear glaze should be described. Tints approaching bright straw and lemon yellows are the ones sought after. Brownish and reddish tints are not acceptable to the trade buying the ware.

The behavior of the glaze on the clay must also be given. From these data the potter will be able to determine whether the acidity of his glaze must be increased or diminished, or which clays to mix, if he chooses to keep the glaze as it is and compensate the incorrect coefficient of expansion of the clays by mixing them.

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