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## LXVII. On the chemical composition of the substances employed in pottery

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## LXVII. On the Chemical Composition of the Substances employed in Pottery. By Mr. R. A. COUPER\*.

ALL kinds of earthenware are composed of two parts, viz. the body and the glaze.

The body is the principal part of the vessel, being the base or foundation, as indicated by the term itself. The glaze is a thin transparent layer of glass which covers the body and fills up its pores, giving it a smooth surface with a polished and a finished appearance.

I. The substances principally employed to form the body of earthenware are, clays of different kinds, flint and Cornish stone.

Clay which constitutes the base of the body of earthenware is distinguished from siliceous earth by becoming plastic when mixed with water, and being very soft and not gritty to the feel; also when burned, it keeps its form, and becomes firm and solid; whereas siliceous earth crumbles into a powder when burned. Clay when intensely heated, as in porcelain manufactories, does not regain its plasticity, which it loses in the burning, although pounded very fine, in which state it is technically termed potsherd.

Clay is obtained naturally from Cornwall, Dorset, and Devonshire, and is the finer particles of decomposed felspar deprived of its alkali.

1. The finest clay (termed *China clay*) used in Britain is obtained artificially from Cornwall, by running a stream of water over decomposed granite, which carries with it the finer particles of felspar, and is then received into catchpools or ponds where it is allowed to subside. The water is then run off, leaving a fine sediment, which is removed and exposed to the atmosphere for four or five months, when it is ready for export. By analysis of this clay previously dried at 212°, I found it to consist of—

	I.	П.
Silica	46.32	46.29
Alumina	39.74	<b>40</b> .09
Protoxide of iron	•27	•27
Lime	•36	•50
Magnesia	•44	
Water and some alkali	12.67	12.67
	99.80	99.82

For the second analysis I am indebted to Mr. John Brown. The more common clays, which are found naturally depo-\* R ad before the Philosophical Society of Glasgow, April 28, 1847, and communicated by Dr. R. D. Thomson, sited, are supposed to have been produced in a similar manner to the china clay; the rains having washed from the hills the decomposed rock into a lake or estuary, where it has subsided and gradually displaced the water, and become in the course of time perfectly firm and solid, forming fields of clay. The clay is found in layers or strata lying over each other, each layer possessing some distinctive property from the other, which renders each clay fitted for a peculiar purpose.

2. Sandy clay (stiff or ball) is the upper layer of clay, and is used by itself for making salt glazed ware; it is well adapted for this kind of ware, in consequence of the considerable quantity of silica or sand which it contains. By analysis of this clay, I found it to be composed of—

Silica .								66.68
Alumina	ι.				•		•	26.08
Protoxic	le of	f ire	on	٠		•	•	1.26
Lime .	•	•		•				•84
Magnesi	а.				•	•	•	trace
Water.	•	•	•	•	•	•	•	5·14
	_					_	Ī	00.00

being previously dried at 212°, specific gravity = 2.558.

3. *Pipe clay* is the second layer, which is used in making tobacco pipes. This clay is not employed in manufacturing earthenware, owing to its possessing the property of contracting more than sandy clay. It was analysed by Mr. John Brown, who obtained—

Silica.			•		•			<b>53</b> •66
Alumina	a .	•		•			•	32 <b>·0</b> 0
Protoxie	de o	of i	ron					1.35
Lime .	•	•	•		•	•		•40
Magnes	ia				•	•		trace
Water	•	•	•	•	•	•	•	12.08
								99.49

4. Blue clay is of a grayish colour, and is considered the best layer of clay in the whole series, owing to its burning perfectly white, and approaching in character nearest to the china clay. As analysed by Mr. John Higginbotham, it was found to consist of—

Silica		•	•	•		•		<b>46</b> •38
Alumina	3	•	•	•				38.04
Protoxi	de	of	iron		•	•	•	1.04
Lime.	•	•	•		•	•	•	1.20
Magnes	ia	•	•	•	•	•	•	trace
Water	•	•	•	•	•		•	13.57
								100.23

also previously dried at 212°. There is a variety of other clays obtained from these fields, which are of less value, and need not be enumerated here, as they are similar in appearance to those already noticed.

5. Red or brown clay, which is very abundant in the neighbourhood of Glasgow, is a surface clay, and contains a large quantity of peroxide of iron, which gives it a deep brown colour. It is of this clay that common black ware, flowerpots, and red bricks are made, which do not require a very high temperature, else they would fuse. The analysis gave—

Silica	•	•				•	49.44
Alumina	•			•			34.26
Protoxide	of ir	on				•	7.74
Lime			•				1.48
Magnesia	•			٩	•	•	1.94
Water .		•	•		•	•	5.14
							100.00

6. Yellow clay is obtained from various parts of the country, and is so called from possessing a yellow colour both before and after being burned, owing to the presence of iron.

By mixing sandy clay and red clay together, we gain an artificial yellow clay, which is often employed.

Yellow clay, as analysed by Mr. John Brown, was found to contain-

Silica			•	•		•	•	•	58.07
Alumi	na	•	•	•	•	•	•	•	27.38
Protox	cide	of	iro	n	•	•	•	•	3.30
Lime	•	•	•	•	•	•	•		•50
Water	•	•		•	•	•	•	•	10.30
Magne	esia		•	•	•	•	•	•	trace
0									
									99.55

7. Fire-clay is also very abundant in this country, and occurs both on the surface and several fathoms under ground. It is termed marl, and is used principally in potteries for making saggars or vessels for placing the ware previous to burning to protect them from the flame; and owing to its coarse particles, which cause the body to be very porous, is well adapted for strong heats: crucibles, or large pots for glass works, in which the glass is fused, are also made from fireclay, as well as bricks known under the name of fire-brick. This clay was analysed by Mr. John Brown, who obtained—

Silica	•	•	•	•		•			66.16
Alumi	na	•	•		•		•	•	<b>22·</b> 54
Protox	ide	of	iro	n					<b>5</b> •31
Lime	•	•	•	•	•				1.42
Magne	esia				•	•	•	•	trace
Water	•	•		•	•	•	•	•	3.14
									98.57

8. *Flint* as used in potteries is first calcined, then waterground, in which state it is used for mixing with clays, and is called slop flint; but for glazes it is evaporated to dryness, and used in the dry state with other articles which constitute the glaze.

9. Cornish stone or granite is water-ground, then evaporated to dryness for mixing in glazes, and is used in the slop state for mixing with clays.

10. Plaster of Paris or gypsum, which is employed in forming the moulds in which certain kinds of pottery are cast, is a native sulphate of lime. It is a very important article to the manufacturer of earthenware, owing to its singular property of parting easily with the clay by the application of a slight heat. Plaster of Paris requires to be dried at a high temperature before using it; but if it is over-dried, it will not again set for making moulds; the drier the stucco the harder are the moulds that are made of it, and they will stand more readily a greater degree of wear. Plaster of Paris casts, as commonly prepared, cannot again be used for the same purpose.

II. The colours used for printing and painting on ware are similar to one another, excepting that the colours for painting may not be so expensive as for printing; both however form an important and extensive part of the materials of a pottery. The manufacturers of earthenware are much occupied with the improvement of the variety and beauty of the colours, as well as of the patterns or styles that are produced, and hence a great emulation exists among those employed in the trade.

1. The blue colour in printing is produced from cobalt, which is used with flint, ground glass, pearlash, white lead, barytes, china clay, and oxide of tin in reducing its strength.

2. The brown colour by ochre, manganese, and cobalt.

3. The black colour by chromate of iron, nickel, ironstone, and cobalt.

4. The green colour by chrome, oxide of copper, lead, flint, and ground glass.

5. The pink colour by chrome, oxide of tin, whiting, flint ground glass, and china clay, which are mixed in various proportions, fused together at a high temperature, then pounded and mixed with oil, when it is ready for the printer's use. For the following analysis of a blue cobalt calx, I am indebted to Mr. John Adam:---

Silica	٠		•	•		17.84
Peroxide of cobalt	•	•		•	•	19.42
Peroxide of iron .	•		•	•		25.50
Water	•	•		•		8.41
Carbonate of lime a	nđ	ma	gne	sia	•	28.45
						<b>9</b> 9•62

The oil that is used for mixing with the colours, is made by boiling the following substances together; viz. linseed oil, rape oil, sweet oil, rosin, common tar, and balsam copaiba in various proportions.

III. It is but recently since a new method has been applied to cause the colours to flow or spread over the surface of the ware. This object is effected by washing the saggars in which the ware is placed previous to its being fired in the glost kiln, with a mixture of—

1. Lime, common salt, and clay slip. Dry flows are also used, which answer equally well, the mixture being sprinkled on the bottom of the saggar. The following are some of those flows:—

2. Lime, sal-ammoniac and red lead.

3. Lime, common salt, and soda.

4. Whiting, lead, salt and nitre.

5. But there is a wash made of lime, clay slip, nitre, salt, lead, in general use for washing all the saggars employed in the glost kiln, which fuses on the inner surface of the saggar, making it perfectly close and not porous, otherwise the gloss required on the surface of the ware would not be obtained.

IV. The colours used in producing the dipt or sponged ware are of a very cheap kind, as it is only for common purposes that they are employed. The colours when used for dipt ware are put on the ware before it is burned; and when used for sponged ware, are put on the ware in the biscuit state. The following are some of those colours:---

1. A black dip is made from manganese, ironstone and clay slip.

2. A drab dip by nickel and slip.

3. A sage or a greenish-blue dip by green chrome and slip.

4. A blue dip by cobalt and clay slip.

5. A yellow dip by yellow clay alone, or a compound of white and red clay, which produces the same results.

6. A red dip is produced from the red or brown clay; but it is not every quality of this clay that will answer, as it requires to burn red.

The first four of these dips are prepared by mixing a little

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of the colouring agent with a quantity of clay slip; whilst the two last-mentioned dips are mixed with water to produce the slip state, in which state they are employed.

V. There are several kinds of bodies manufactured; but they may be all classed under two heads, viz. porcelain and earthenware.

1. Porcelain or china is a rich, very smooth and transparent ware, and is the finest quality that has yet been manufactured. It is a fused body, and owes its transparency to this circumstance; it also requires a very high temperature to burn it, and is manufactured in this country from flint, Cornish stone (granite), china clay, and bone-earth; the lime employed acting as a flux, partly fusing it. By analysis of two pieces of china from different manufactories in Staffordshire, I found them to be differently composed. The last of these pieces was also analysed by Mr. Crichton, the three analyses being as follows:—

No. 1, by R. A. C.	No. 2, by R. A. C.	No. 2, by W.C.
Silica	40.60	39.685
Alumina	24.12	24.620
Lime 10.06	14.22	14.176
Protoxide of iron $26.44$ Phosphate of lime $26.44$	15.32	15.386
Magnesia	•43	•311
Alkali or difference 2.14	5.28	5.792
100.00	100.00	100.000

2. Foreign manufacturers do not employ bone-earth; but instead of it they use felspar, the alkali of which supplies the place of the phosphate of lime. The Germans make the best porcelain for chemical purposes, as that body is more vitrified and less liable to be acted upon by acids, as well as being capable of standing a very strong heat; and hence it is extensively used by chemists. By the analysis of some specimens of foreign porcelain, I obtained the following results :--

Berlin. Chinese Porcelain, superior. inferior. Silica 72.96 71.04 68·96 Alumina and protoxide of iron 24.7822.46 29.24 Lime . 1.04 3.821.60 Alkali 1.22 2.68 100.00 100.00 99.80 Specific gravity 2.4192.314 2.314 ٠

VI. Earthenware is a very porous and less compact body than china or porcelain, owing to its containing little or no alkali, which is the great difference between these bodies. I had a piece of ware manufactured, resembling in appearance porcelain, as regards the absence of porosity and its compactness, slightly transparent, and capable of standing a very strong and sudden heat; it was produced by mixing soda to the extent of  $3\frac{1}{2}$ per cent. in a little clay prepared for the common white body, and was then fired in the biscuit kiln. The clay employed having been previously well dried, so as to weigh it without water, the proportional quantity of soda requisite was then calculated and weighed out; the clay was again mixed with water along with the soda; it was then formed into capsules, which after being fired and then broken, presented the appearance of a vitrified or fused body.

1. The common white ware or earthenware is made from flint, Cornish stone, china clay, and blue clay, and does not require such a high temperature in burning as the porcelain does. By analysis of a piece of white ware manufactured in this city, it was found to contain—

Silica	•	•	•	•	•		68 <b>•</b> 55
Alumina and pro	otox	ide	of	irc	n	•	29.13
Lime	•	•	•	•	•	٠	1.24
							98·92
Specific gravity	•	•	•	•	•		2.36

Coloured ware is also manufactured from the same substances, but mixed with a colouring agent which stains the body.

The toqua or blue-coloured ware is coloured by cobalt.
The sage or greenish-blue coloured ware, by nickel and

cobalt.4. The drab or buff-coloured ware by chromate of iron.

5. The body for the cane or yellow-coloured ware is produced by a mixture of sandy clay and common red clay, the same as used for red bricks, but is generally produced from the natural yellow clay found in particular localities.

6. The last-mentioned body is also employed for making Rockingham ware, which only varies from the cane ware by possessing a different glaze.

7. The common black ware body is made from the red clay alone.

8. The Egyptian ware body is made from ironstone, ball and red clay.

These four last-mentioned bodies are not nearly so expensive as the white ware, and do not require nearly such a high temperature to burn them; therefore they are, comparatively speaking, soft bodies.

9. Salt glazed ware is made from sandy clay and a little sand, to keep the body open, or make it less compact; but for large salt glazed ware, potsherd, which is ware that has

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been fired and then ground, is employed to render the body still more open or porous, and also to give it a greater capability of standing sudden heats or colds. This ware is much used in public works for chemical purposes: it is exposed to the action of the flame during burning, whereas other kinds of ware are protected by saggars from the flames.

VII. The glaze vitrifies the surface of the body, rendering it generally capable of withstanding acids. It is a very important point with the manufacturer to obtain a glaze which will adhere to the body without crazing or peeling off, as he may discover a good body, but not find a glaze to answer it, since every glaze will not adhere to the same body, and hence every manufacturer has a glaze of his own composition.

1. The substances used in the preparation of the glaze for white ware, are borax, china clay, flint, Cornish stone, Paris white, and white lead.

In preparing the glaze, a substance technically termed frett is first made, consisting of borax, china clay, flint, Cornish stone, and Paris white, which are fused together in a kiln, and when ready allowed to flow into water, which shortens it, owing to the water being mechanically lodged in it, and keeps it from adhering to the bottom of the vessel, rendering it much easier to pound. Frett is a beautiful glass, coloured by a little iron, and is pounded and water-ground along with Cornish stone, flint, and white lead: this constitutes the glaze for white ware.

				,	Analysis of white glaze.	Analysis of frett.
Silica			•		43.66	55.98
Lime :	•		•	•	•52	2.52
Alumina and protox	ide	of	ire	on	9.26	10.38
Borax					20.08	31.12
Carbonate of lime	•	•	•	•	10.88	
Carbonate of lead	•	•			15.19	
					99.89	100.00
Specific gravity .	•	•	•	•		<b>2·</b> 345

A piece of earthenware was brought from America, having been discovered several feet under ground, the glaze of which was tested, and found to be composed of silica, iron, alumina, lime, sulphate of lime and antimony, which was a beautiful rich white glaze concealing a common red clay body.

2. The glaze of Rockingham ware possesses a beautiful brownish metallic lustre, and is made from Cornish stone, flint, manganese, red lead and clay slip, the latter substance being a little clay mixed with water until it becomes of the consistency of milk.

3. The glaze for common black ware is made from the same

materials in different proportions, and has a brilliant black appearance.

4. The glaze used for cane or yellow-coloured ware is made from flint, red lead, and Cornish stone.

5. The Egyptian ware owes its value to the beautiful and rich tinted black glaze, made from flint, Cornish stone, red lead, and manganese, with which it is covered.

These four last-mentioned glazes are made by stirring the substances together with a certain quantity of water, and passing it through a very fine sieve or search. Glazes do not require such a high temperature to fuse them on the surface of the ware, as the body does to be burned.

6. The glaze for salt glazed ware is common salt, which is thrown in at the top of the kiln through a number of small apertures in the crown of it, and diffuses itself through all parts of the kiln, giving the ware the required glaze. The action that is supposed to take place, when the salt is thrown into the kiln, is owing to its decomposition. The chlorine of the salt combines with the hydrogen of the water, which is mechanically lodged in the salt, forms muriatic acid gas, which passes off, while the sodium combining with the oxygen of the water then unites with the silica in the ware, forming a silicate of soda which fuses on its surface. The salt is not thrown in until the kiln has been raised to its greatest necessary temperature.

Table	of	the	Composition	of	Clays	and	Porce	lain	when	free
			fror	n '	Water,					

	Silica.	Alumina.	Protoxide of iron.	Lime.	Magnesia.	Phosphate of lime and protoxide of iron.	Alkali and loss.	Specific gravity.
Cornish china clay Cornish china clay Sandy clay Pipe clay Blue clay Red clay Fire clay Yellow clay	53.16 53.12 70.29 61.39 53.52 52.11 69.33 65.06	45.61 46.00 27.47 36.61 43.89 36.19 23.62 30.68	·31 ·31 1·33 1·54 1·20 8·17 5·56 3·70	·41 ·57 ·90 ·46 1·39 1·56 1·49 ·56	·51 ·51 Trace Trace 2·04 Trace Trace Trace	•••••		2.558
English china ware, No. 1 No. 2 Berlin ware Superior Chinese ware Inferior Chinese ware Common English white ware	39.88 40.60 39.68 72.96 71.04 68.96 68.55	21·48 24·15 24·65 24· 22· 29· 29· 29·	78 46 24 13	$10.06 \\ 14.22 \\ 14.18 \\ 1.04 \\ 3.82 \\ 1.60 \\ 1.24$	Trace •43 •31 Trace Trace Trace Trace Trace	26·44 15·32 15·39 	2·14 5·28 5·79 1·22 2·68	2·419 2·314 2·314 2·360