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Official Notices.

APPOINTMENT OF HON. TREASURER.

Mr. THOMAS TYRER, Stirling Chemical Works, Stratford, London, E., has been appointed Hon. Treasurer of the Society. Subscriptions may now be sent to him.

ANNUAL INDEX, 1907.

The Index is issued with this number of the JOURNAL.

DRAFT BY-LAWS.

AS FINALLY SETTLED BY THE COUNCIL.

TAKE NOTICE that in pursuance of the provisions of Clause 37 of the Charter a General Meeting of the Society will be held at the House of the Society of Arts, John Street, Adelphi, London, on Friday, the 13th day of March, 1908, at 3.30 o'clock in the afternoon, for the purpose of considering and adopting the draft By-laws, which, after due consideration of the observations received from members in response to the invitation in that behalf, have been finally settled by the Council, and a print of such finally settled By-laws was sent to each Member of the Society in the January 31st number of the JOURNAL.

By order of the Council.

CHARLES G. CRESSWELL,
Secretary.

Birmingham and Midland Section.

Meeting held at Birmingham on Thursday, November 28th, 1907.

MR. HARRY SILVESTER IN THE CHAIR.

THE VALUATION OF FIRECLAYS.

BY E. P. PAGE AND W. J. REES.

The chemical and physical properties of the naturally and artificially formed silicates have received, and are at the present time receiving considerable attention both by mineralogists and technical investigators, the first mentioned dealing with the various questions from the geophysical standpoint, and the latter having more regard to the formation of slags, glazes, &c., in industrial operations. In both cases the research has more particular reference to the reactions taking place in the liquid or viscous states. The clayworker studies the question, we may say, from three standpoints, as follows:—

1. The production of silicate compounds fusible at temperatures from 900° to 1500° C., as glazes.
2. The production of partially fusible bodies, as porcelain (*i.e.*, bodies which "mature" at certain definite temperatures).
3. The production of bodies as infusible as possible, for the building of ovens and furnaces for use in the various industries whose processes necessitate the use of high temperatures.

In the first case mentioned, the mixture of the various compounds is heated until it is in a liquid state, and there is opportunity for interaction of the constituents.

In the second case, only a partial reaction is permissible, and heat is applied just sufficiently to bring about this reaction.

In the third case, the less reaction there is between the constituents the better. This last instance is the only one with which we are immediately concerned, and the purport of this paper is to indicate some of the factors which have to be taken into account when considering the utility of a fireclay.

As a preliminary, we may say that clay workers think of temperatures in the Seger cone scale, and not particularly in thermometric degrees. The cone scale is used in this paper, though we give the approximate temperature

at which the cone is supposed to melt. A recent test of these cones shows that, although there are differences of 10° C. in some cases between the theoretical and actual melting points of cones, yet a series of any one number are fairly accurate in themselves. Further, that a clay cannot be considered as "refractory" which is not equal in fire-resisting properties to cone 26 (about 1650° C.). The rule adopted by the Association of Firebrick Manufacturers in Germany is as follows:—"The limit of refractoriness of a material is to be considered as exceeded when the material, or one of its constituents, uniformly distributed in fragments, begins to melt or separate by liquation; not only the surface of the piece tested, but also the face of the fracture must be taken into consideration when judging." There is no such standard in this country, neither does there seem to be any recognition of the potentialities in the manufacture of refractory articles. Some people have a fancy for the productions of a certain district or a particular mine, others consider one clay is as good as another, and consider the price of purchase only. The appearance counts for much with some, and finally the chemical analysis is considered a criterion by which to judge.

The following data are necessary for a complete examination:—Chemical analysis; mineralogical analysis; mechanical analysis; specific gravity of the fired wares; porosity; limit of refractoriness; behaviour of the clay when fired at intervals from cone 1 to cone 10. With this information at hand, one may form a fair idea as to the value of refractory materials for different purposes. It must be borne in mind, however, that no single clay will make articles to suit every purpose. Success can only be obtained by the building up or synthesis of bodies from materials often widely differing from each other.

Chemical analysis.—It is not necessary to go into the details of the methods of analysis, but rather to indicate some considerations as to the use of the ultimate chemical analysis in affording data for estimating the value of a clay for any given purpose. It is, of course, of value as indicating the presence or absence of any deleterious substances. A large proportion of fluxing impurities such as iron oxides, lime, titanium, alkalis, &c., will naturally seriously discount the value of a fireclay. The usual method of using the ultimate analysis is to consider only the ratio of total fluxes to silica. Richter, Bischof, and Seger have all, many years ago, shown this to be very unsatisfactory, as it left the alumina contents of the clay entirely out of consideration. They showed that the primary ratio to be taken into consideration is that of silica: alumina, and that it is the ratio of total fluxes to this ratio which is important. Richter, in 1868, pointed out that the extent to which any fluxing constituent lowered the fusing point was directly proportional to its molecular weight. On this principle, both Bischof and Seger deduced formulæ for calculating the refractoriness from the ultimate analysis. A formula of this kind is as follows:—

$$\frac{(\text{Percentage of alumina})^2 \times \text{Mol. wt. of alumina}}{(\text{Mol. wt. of silica})^2 \times (\text{Percentage of silica}) \times F}$$

where F is the sum of the percentages of the fluxes divided by their respective molecular weights.

Ludwig has gone still further in this direction, using the general law applying to dilute solutions (first enunciated by Richter as previously referred to), that equimolecular quantities of different substances dissolved in equal amounts of the same solvent, lower the melting point in the same degree. Ludwig, assuming the clay as the solvent and the fluxes as the dissolved substance, calculated the molecular formula of a clay from its ultimate analysis, making the alumina equivalent equal to unity and adding together the equivalents of the various fluxes, thus obtaining a formula such as $\text{Al}_2\text{O}_3, 2.125\text{SiO}_2, 0.0755\text{RO}$. In this expression there are only two variables, silica and flux (RO). This molecular formula

CHART SHOWING LUDWIG'S METHOD.
CLAYS FROM TABLE N°1 INDICATED BY●AND N°. CONES BY○AND N°.

is then plotted on a chart, the silica as the abscissa and ten times the equivalent of the fluxes as the ordinate. The melting point zones on the chart were obtained by calculating the molecular formulae for Seger cones 28 to 39, and plotting them as before. The origin was then assumed to be pure alumina, and the equivalent amount of flux which it was necessary to add to an equivalent of alumina in order to lower its melting point to that of any given cone was determined by experiment. This amount of flux was then marked on the ordinate, and a line drawn from that point to the abscissa, passing through the given cone point on the chart. Richter's law strictly speaking, applies to dilute solutions only, hence this formula and chart are more applicable to clays with but a small amount of flux, and do not apply to common

brick clays and glazes. The method is certainly, at the present time, the most useful way of applying the results of the ultimate analysis, though the examination of a number of fireclays shows it to be not altogether reliable (See clay No. 2 in table of analysis). The point where these formulae break down, to some extent, is in their failure to bring into consideration the mechanical constitution of the clay. For instance, the exact state of the presence of the silica in the clay is very important. If it is in a fine amorphous state, it may lead to fluxing, whilst if it is in comparatively coarse particles it renders the clay more refractory. From the above considerations it is obvious that the ultimate chemical analysis is insufficient, and though, of course, very much better than no test at all, is at times totally misleading.

No.	Percentage Composition.						Formula, $Al_2O_3 = \text{Unity}$.						Sum of formula.	Melting point.	
	SiO_2 .	Al_2O_3 .	Fe_2O_3 .	CaO .	MgO .	K_2O .	SiO_2 .	Al_2O_3 .	Fe_2O_3 .	CaO .	MgO .	K_2O .		Cone.	Chart.
1	70.70	25.80	2.38	.31	—	.89	4.050	1	.1166	.0219	—	.0347	$Al_2O_3, 4.656 SiO_2, .176 RO$	29—30	30—31
2	73.84	20.54	4.43	.08	—	1.40	6.112	1	.2745	.0069	—	.0060	$Al_2O_3, 6.112 SiO_2, .288 RO$	19—20	28
3	63.09	43.21	2.43	.11	.28	.37	2.124	1	.0717	.0045	.0165	.0002	$Al_2O_3, 2.124 SiO_2, .102 RO$	33—34	34—35
4	73.07	21.74	3.50	.41	.26	1.0	5.71	1	.2053	.0343	.003	.050	$Al_2O_3, 5.71 SiO_2, .293 RO$	31—32	28—29
5	68.60	29.10	3.75	.45	.29	.790	4.45	1	.047	.008	.007	.008	$Al_2O_3, 4.51 SiO_2, .273 RO$	32—33	29—30
6	74.43	20.21	3.15	.43	.18	1.2	6.13	1	.193	.0396	.0198	.0044	$Al_2O_3, 6.13 SiO_2, .317 RO$	31—32	27—28
7	64.90	30.25	3.05	.47	.69	.49	3.65	1	—	.230	—	—	$Al_2O_3, 3.65 SiO_2, .230 RO$	32	30—31
8	67.50	27.95	2.55	1.22	1.25	.25	3.05	1	—	.270	—	—	$Al_2O_3, 3.05 SiO_2, .270 RO$	29	29—30
9	45.08	38.54	.90	.08	.38	.66	2.015	1	.0298	.0037	.0254	.0186	$Al_2O_3, 2.015 SiO_2, .0775 RO$	35	35
10	47.69	38.15	.077	.21	TiO_2 .12	1.26	2.125	1	.0257	.0100	TiO_2 .0040	.0358	$Al_2O_3, 2.125 SiO_2, .0775 RO$	35	35

"Rational" analysis.

	Clay No.									
	1	2	3	4	5	6	7	8	9	10
Clay substance— $Al_2O_3, 2SiO_2, 2H_2O$	62.42	53.83	64.03	51.31	62.07	48.27	—	—	96.55	—
Felspar— $K_2O, Al_2O_3, 6SiO_2$	4.81	1.30	5.07	4.92	1.52	4.62	—	—	1.15	—
Quartz sand— SiO_2	32.77	44.87	—	44.10	36.41	47.11	—	—	2.30	—

Mineralogical analysis.—Fireclays and shales consist of varying amounts of quartz, silica (sand), silicate of alumina (clay substance), and feldspathic matter in the shape of sand, and in many cases mica. Seger worked out a method for the separation and determination of these three main constituents by treatment with sulphuric acid and caustic soda to remove the clay substance; the residue is then treated for the determination of alumina, iron, and alkalis, and from the figures obtained the mineralogical composition is calculated. To arrive at comparable results, standard solutions should of course be used. Seger did not claim that the method was strictly scientific, but it is most useful, and gives good practical information. The assumption that the felspar present is orthoclase does not always hold good, neither can one say that it is always insoluble in sulphuric acid. Hydrated silica may also be present, and would be included in the figures as clay substance, but, in spite of these facts, as already stated, clay workers find the information of much use, and in considering refractory clays it enables them to anticipate to some extent the probable behaviour of the clays at high temperatures. This will be seen if we consider the phenomena of fusion. The first step in the destruction of a clay is the softening of the most fusible constituent, usually the felspar, this fused constituent then reacts with the others and leads to the formation of more fusible compounds, until finally the whole mass loses its shape. It is a point as to the order in which this fluxing action continues after the fusion of the most fusible constituent. Assuming, for the moment, that in a given clay the felspar is the most fusible, it is not quite certain whether the clay substance or the silica is first attacked. It will largely depend, first on the purity, and then on the size of the particles.

Mechanical analysis.—From the last statement it will be seen that the nature of a clay, whether of a fine or coarse structure, has some bearing on its behaviour under working conditions. The clay is first broken down by boiling, and an examination of the coarser particles is made microscopically. To obtain definite information and measurements of the grains, recourse must be had to elutriation. This can be done approximately with the Schultz apparatus, or more accurately with the Schoene or centrifugal apparatus. (For description of this latter apparatus see Bull. 64, Bureau of Soils, Dept. of Agriculture, Washington, U.S.A., 1900.)

The results of such an examination with the Schoene apparatus are set out below:—

	A.	B.
	Per cent.	Per cent.
Coarse sand, grains over 0.333 mm.	0.68	0.39
Fine " " from 0.333 to 0.040 mm.	3.41	20.95
Silt " " from 0.025 to 0.010 mm.	3.81	14.13
Rock dust from 0.025 to 0.010 mm.	10.92	20.17
Clay substance from 0.010 to 0.000 mm. ..	81.51	38.55
	100.33	100.10

A is a fat, plastic, refractory fireclay. B is a lean, short clay.

Specific gravity and porosity.—These factors are of use as indicating the structure of the manufactured article, and have more particular application to special productions, such as crucibles, &c. A porosity determination is generally considered the most useful. At the present time two methods of expression are used. In one, the degree of porosity is expressed as the percentage of water absorbed by a given weight of dry brick. In the other and most rational method, the expression of porosity refers the volume of pore space to the volume of the brick. The term specific gravity is also used ambiguously, it is used as expressing the specific gravity of the clay, as determined by grinding to powder and using the ordinary method for insoluble powders, and it is also used to express the volume weight of the whole piece. This question is well treated in Jackson's "Ceramic Calculations."*

* Longmans, Green and Co.

Limit of refractoriness.—A definition of what is meant by the limit of refractoriness was given in the first part of this paper. It now remains to speak of the methods and value of the determination. One of the first methods used was an indirect one; it consisted in mixing pure quartz sand with the clay to be tested, and determining the proportion of sand necessary in order that the test piece should run down to a liquid at the same temperature as a standard clay. This was not satisfactory. Bischof then adopted standard clays as a means of comparison, but as the standard clays were not available to others, Seger adopted mixtures of silica and alumina, &c., forming the mixture into "cones" or small pyramids. The most modern method is to expose the clay to the high temperatures obtainable in the electric furnace, and we believe this is the method adopted at the National Physical Laboratory; it is claimed that it gives a much more accurate result than the use of the Deville furnace and Seger cones as standards. This may be, but as far as we are aware, no direct comparison has been made between the two methods. As pointed out, one does not necessarily want to know the limit of refractoriness in thermometric degrees. There are influences other than temperature to be taken into account when considering the probable behaviour of clays in actual practice. Furnace gases, dust, and the time factor enter into question; therefore, a comparison with standard mixtures of comparative purity, for the same interval of time, the same furnace atmosphere and temperature, which is obtained by the use of a combustion furnace, such as the Deville, is of greater value than the knowledge that the limit of refractoriness is so many degrees Centigrade.

It was mentioned that the minimum of refractoriness was cone 26, and the maximum it is worth noting is about cone 36, which is the figure for pure kaolinite, quartz being nearly as high. Fireclays having a refractoriness equal to cone 35 are very scarce, and consequently somewhat high in price.

Behaviour in fire.—The value of this factor is in the information it affords as to contraction and expansion at various temperatures. This information is more particularly useful to the manufacturer.

In conclusion, we may say our intention was not to treat the points exhaustively, but rather to indicate some of the necessary data which must be available before an opinion can be formed as to merits or demerits of various clays, and finally we wish to express our thanks to Messrs. E. J. & J. Pearson, Ltd., and to Messrs. Chance Bros. & Co., Ltd., for permission to use the information given.

DISCUSSION.

The CHAIRMAN said that only that week a case of considerable loss had come under his notice, whereby a quantity of finished iron was spoiled through the use of an inferior firebrick, which was unable to withstand the temperature to which it was exposed. Any method, therefore, which afforded a ready means of testing the refractory properties of fire-resisting materials and determining their suitability or otherwise for various purposes, should be of technical interest and value.

With reference to the presence of spots of iron oxide in fireclay goods, which frequently caused a failure at high temperatures, he asked the authors if in their experience the weathering of the clay got rid of the iron, and improved its refractory qualities.

Professor T. TURNER said that testing of fireclay was of great importance in the Midland district, but hitherto there had been no uniform and recognised method adopted in this country for the testing of fireclay. In recent years, however, and particularly since the establishment of the Pottery School in North Staffordshire, a number of important investigations had been carried out by English workers. The Schöne apparatus for the mechanical analysis of clays had been introduced into the North Staffordshire Pottery School with very satisfactory results. Reference might also be made to a method of recording the size and physical properties of moulding sands which had recently been described by Prof. Ries. In this system, a series of tests and standards was adopted, including fineness, permeability, porosity, refractoriness,

binding properties, chemical analysis, and duration of use. These properties were then diagrammatically represented on a card, so that any other sand could be at once compared with one which had been already tested.* Possibly some such method might be found applicable in the clay industry. In connection with sizing by means of sieves attention was drawn to the work of a Standardizing Committee of the Institute of Mining and Metallurgy, as a result of which wire meshes of accurate gauge and of definitely progressive sizes would very shortly be obtainable; and for scientific purposes such screens should replace the unsatisfactory wire gauze now in general use. The interesting series of shrinkage tests exhibited by the authors had, no doubt, a direct bearing on the irregular results which were obtained at high temperatures with the old Wedgwood pyrometer.

Mr. L. ARCHBUTT asked whether the authors could give any information as to the composition of firebricks best able to resist the fluxing action of coal ash; also whether the time factor was not of considerable importance in the use of Seger cones, and the best method of using these cones as temperature indicators, in controlling pyrometers for example.

Mr. H. L. HEATHCOTE said he would like to know more about the chemical and physical properties associated with the absence of cracking in articles made from fire-clay.

Mr. E. A. LEWIS asked if the "weathering" of fireclay had anything to do with its properties.

Mr. COLLIS said that he also had heard that weathering was of importance.

Mr. WHITELY referred to the usefulness of the microscopical work on the structure of fireclay bodies by J. W. Mellor.

Mr. E. P. PAGE said, in reply to Prof. Turner, that silica might be considered a high temperature flux, and the other fluxing compounds present might be considered low temperature fluxes.

The action of flying ash was a serious problem with the use of rotary cement kilns, the linings of which were subject to the action of ash and of the cement. A thin coating of "diamantin" or of "carborundum" had been recommended; some works used a brick with as little "free" silica as possible, whilst bricks with a fair amount of silica (65 to 70 per cent.) were considered by others to be satisfactory.

Weathering of clay brought it into a condition much more easy to work, and saved much wear and tear of grinding mills. First-class bricks were being made from unweathered clay by proper methods of working up the clay.

* Proc. Amer. Foundrymen's Assoc., 1906, p. 63.

London Section.

Meeting held at Burlington House on Monday, January 6th, 1908.

DR. J. LEWKOWITSCH IN THE CHAIR.

THE DETERMINATION OF SMALL QUANTITIES OF BISMUTH.

BY HERBERT W. ROWELL.

The accurate determination of small quantities of bismuth in copper, lead, and several alloys used in electrical and chemical work and in the raw materials from which they are made, has of late developed further importance to many connected with these industries, but experience has shown that concordant results are not obtained by the usual methods of analysis, and the discrepancies are a source of much inconvenience. In illustration, the following are results found by various

chemists on the same samples of base bullion, with the expectation of agreeing within 0.005 per cent. :—

Chemist:	A	B	C	D	E	F
Sample	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
No. 1	0.155	—	0.002	0.125	—	—
" 2	0.080	0.054	0.008	—	—	—
" 3	0.095	—	0.003	—	0.083	0.062
" 4	0.110	0.062	—	—	0.090	—

It is usual to separate bismuth as a basic salt and weigh as the tri-oxide, basic chloride, or metallic bismuth, but as the conditions for completely precipitating these basic salts are not easily secured without at the same time including other metals, the results vary widely on either side of the truth.

Stone (this J., 1887, 416) points out that excess of potassium iodide added to a dilute sulphuric acid solution of bismuth produces a yellow colour, the intensity of which is directly proportional to the amount of bismuth present, and the figures at the end of this paper further show that it is possible to estimate small amounts with great delicacy even in the presence of many other elements. Unfortunately, the methods of arriving at a solution containing all the bismuth free from other metals present many difficulties, upon which no light has been thrown, and which are generally unnoticed. The notes following are the result of much practical work and point out some usual sources of error with means of avoiding them.

Bismuth is precipitated as sulphide from dilute hydrochloric and sulphuric acid solutions by hydrogen sulphide; the precipitate is soluble in strong hydrochloric acid and in nitric acid and other oxidising agents, and is slightly soluble in ammonia and ammonium sulphide, but is precipitated by and insoluble in excess of dilute sodium or potassium sulphide solution, and by these means may be separated from all usually occurring metals except lead, copper and silver. The silver may be precipitated from moderately acid solutions by hydrochloric acid or sodium chloride, and will leave all bismuth in the filtrate. It is often stated that bismuth is carried down when precipitating large quantities of lead from the solution as sulphate. This, however, is not so if the solution contains a sufficient quantity of nitric acid, and the lead is precipitated gradually from the boiling solution to prevent occlusion. To obviate this supposed loss, Low and others attempt to precipitate the bismuth as basic chloride from a nitric acid solution of refined lead, by adding dilute ammonia till free acid is neutralised and the liquid remains faintly opalescent, and then adding 1 c.c. of dilute hydrochloric acid. The neutralisation is difficult to perform to this degree of nicety, and when the acid is added it is seized by the local lead and bismuth, which it converts into insoluble basic chlorides, and the main portion of the bismuth is either precipitated as hydroxide or basic nitrate, or, as more often happens, remains in solution. When it is necessary to evaporate a solution of lead, bismuth, &c., to fuming with sulphuric acid, the residue should be well boiled with a liberal quantity of dilute sulphuric acid, as the lead sulphate retains a large proportion of a form of bismuth sulphate which is not easily soluble. Bismuth salts are not volatile at the temperature of boiling sulphuric acid, and the loss, recorded by Brearley and Ibbotson, in the presence of antimony must have been mechanical. Ulgreen separated large quantities of lead from bismuth by depositing the latter on a strip of pure lead immersed in the acetic solution, but a small quantity of bismuth is not all deposited after 24 hours, and there is still the strip of lead to be got rid of.

In the absence of lead, any silver and copper may be separated from a sulphuric, nitric, or acetic acid solution by precipitating them with an excess of potassium iodide, boiling, cooling, and shaking to collect the fine precipitate and filtering, or the bismuth may be separated as oxychloride as directed below, after removing the silver as chloride. The separation of bismuth from copper as a double cyanide with potassium is uncertain in the case of small amounts. The separation from copper, adopted