

An Investigation of the Spectra of Flames Resulting from Operations in the Open-Hearth and "Basic" Bessemer Processes

W. N. Hartley and Hugh Ramage

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X. *An Investigation of the Spectra of Flames resulting from Operations in the Open-hearth and "Basic" Bessemer Processes.*

By W. N. HARTLEY, *F.R.S.*, *Royal College of Science, Dublin*, and HUGH RAMAGE, *A.R.C.Sc.I.*, *St. John's College, Cambridge.*

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IN the 'Philosophical Transactions' for 1894 were published Parts I. and II. of "Flame Spectra at High Temperatures, the Spectrum of Metallic Manganese, &c.," and Part III. "The Spectroscopic Phenomena and Thermochemistry of the Bessemer Process." The results obtained by one of us up to 1895 had reference to the phenomena observed in flames seen to issue from the vessels in which are carried on the operations of the "acid" Bessemer process. The following account deals with an investigation of the Thomas-Gilchrist or "basic" process.

Works in various parts of England were visited in order to ascertain where suitable observations could be made without incurring serious personal risks or damage to instruments, and to obtain permission to carry on these investigations.

5.6.1901.

The Cleveland district of Yorkshire was chosen as the principal centre, owing to the interest taken in the work by Mr. ARTHUR COOPER, Managing Director of the North-Eastern Steel Company, and, in consequence of the courtesy and attention shown us, the North-Eastern Steel Works at Middlesbrough were selected.

It was found necessary at the outset to have three observers at work simultaneously. Twenty-eight plates of photographs and copious notes were taken successfully, with photographed spectra to the number of about 140.

According to previous experience it was found advisable to obtain photographs of the flame, sparks and fume at different stages of the "blow," as well as photographs of spectra. These were executed with a small Anschütz camera and Goertz lens, giving excellent pictures with very rapid exposures. Some of the photographs of spectra could not be surpassed with the dispersion of the instrument employed, but the work was not accomplished without some difficulty, which was occasioned by the large quantity of lime dust blown into the air.

The results were quite different from those previously obtained; for instance, many lines and bands quite new to the Bessemer flame have been recognised in addition to the spectra of the common alkali metals, iron, and manganese.

Thus rubidium, caesium, calcium, copper, silver, and gallium have been identified. Very careful analyses of the crude metal, the ore, and lime, and also of the rail steel manufactured, were made for the purpose of separating some of these substances and identifying them subsequently by a spectrographic observation of the separated bases.

The technical importance of being able to ascertain the amount of phosphorus in the metal during the process of "blowing" made us very desirous, if possible, of determining this. Notwithstanding that the work has been continuously in progress since 1895, and that every line and band in the different spectra photographed has been accounted for, our observations so far have failed to yield information or even any indication of when the blast should be stopped. The cause is not far to seek if we bear in mind that phosphorus existed in the pig-iron probably as a ferrous phosphide, which, according to previous experiments, is not volatilised, and that at a high temperature in contact with a powerful base like lime and in presence of air it becomes a non-volatile calcium phosphate or a ferrous phosphate. Nevertheless, some insight into the chemistry of the process of the "blow" has been obtained. The greatest interest is attached to the knowledge it has given us of flame spectra under variations of temperature and of the wide distribution of many of the rarer elements in minute proportions in ores and common minerals ('Roy. Soc. Proc.,' vol. 60, pp. 35 and 393; 'Chem. Soc. Trans.,' 1897, pp. 533 and 547).

As we have had the honour of laying before the Royal Society and also the Chemical Society accounts of some of our results, there is no necessity to make more than an incidental allusion to them.

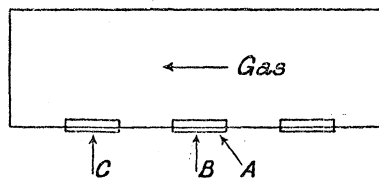
We have also sought for the spectra of metals in the open hearth steel furnace, and propose to very briefly record here our want of success in this direction.

The Siemens-Martin Furnace.

The investigation was made, by the kindness of Mr. F. W. WEBB, in the steel works of the London and North-Western Railway Company, Crewe, in the first week of January, 1895.

The steel melting furnace No. 3 had been charged with 15 tons of old rails at 11 P.M. on January the 2nd. The observations were made from about 10 A.M. on the 3rd January. Eye observations were first made with a direct-vision spectroscope through one of the charging doors of the furnace; the charge was perfectly fluid, and was covered with slag, through which bubbles of gas escaped. The charge was ready for tapping about 3 P.M. on the same day. The only line seen in the spectrum of the light emitted by the gas above the charge and the furnace wall beyond was the yellow line of sodium seen as one bright line; the continuous spectrum was very strong. Photographs of the spectrum were then taken to obtain a permanent record and to discover how far the spectrum extended towards the ultra-violet.

Plate 1.—A Cadett plate stained with erythrosin after McCLEAN'S method.



Four exposures were made with the instrument pointing as indicated in the above plan of the furnace, and about 3 yards away from the door. The spectrum extended to the wave-lengths here recorded.

		λ .
1.	Pointed as in A, $\frac{1}{2}$ min. . . .	3800
2.	„ „ „ 2 mins. . . .	3540
3.	„ „ B, 1 min. . . .	3720
4.	„ „ „ 3 mins. . . .	3470

Plate 2.—THOMAS'S "Sandall" plate stained with erythrosin. Same direction as B, the slit being about 4 feet away from the door in the first, and about 3 yards in the second, third, and fourth photographs.

		h.	m.	s.		h.	m.	s.	λ .
1.	Exposed from	11	27	10	to	11	29	10 3590
2.	„ „	11	31	0	„	11	35	0 3565
3.	„ „	11	36	50	„	11	38	50 3700
4.	„ „	11	39	10	„	11	39	25 —
5.	Solar spectrum for reference.								

For 3 and 4 the spectrograph was pointed as in C.

Plate 1 was very sensitive to the greenish-yellow and yellow rays, but it shows no trace of the sodium lines. The spectra are very strong in the blue and violet, but fade gradually towards the extreme violet, and thence to the wave-lengths recorded above.

It must be remembered that the flame playing across the hearth of the furnace, although at a very high temperature, is oxidising, and, as will be seen later (p. 498), it should, at the most, give only feeble spectra of such elements as lithium, potassium, calcium, and, we should infer, iron and probably manganese. The carbon monoxide as it escapes from the bath of metal and slag would, however, tend to intensify the spectra of these metals, and care was taken to turn the collimator in a direction parallel to the surface of the bath and as near to its surface as the opening for the door would allow.

The temperature of the gas must be higher than the temperature of the walls of the furnace which are heated by it, hence the fact of the sodium line being bright is in accordance with KIRCHHOFF'S law.

Observations on the Flames from a Cupola Furnace.

While at Crewe Works, eye observations were made on the spectra of the gases passing the opening of a cupola through which the charge was introduced. Pig-iron was being melted in the cupola for the "acid" Bessemer process, while the blast was turned on the flame was bluish, and lines of sodium, lithium, and potassium were detected; the latter were very weak. When the Root's blower stopped, the flame became smaller and whiter, and the lines of the above elements became stronger; the ends of the two strongest bands of manganese were also seen. There was, doubtless, a large proportion of reducing gas in the flame in the latter case.

Description of the "Blow" and "Over-blow" in the "Basic" Bessemer Process at Middlesbrough.

The vessel is first charged with about 2 tons of lime in lumps, and then with 12 tons of fluid "mixer metal." The blast is turned on, and the vessel rotated into a nearly vertical position.

The iron used for the basic Bessemer process in the works is a mixture of fluid metals coming direct from the blast furnaces with molten pig-iron from a cupola, the two fluids being completely mixed and in such proportions that the composition of the mixture is practically constant; it is thus rendered suitable for uniform treatment. This, which is technically known as "mixer metal," is poured out of a Hoerder mixer into a ladle, which delivers it into the converter; this "mixer metal" usually contains—

Manganese	about	1·0	per cent.
Silicon	„	0·6	„
Phosphorus	„	2·5	„
Sulphur	„	0·08	„
Carbon	„	3·4	„

The blow may be divided into three stages. The first stage ends when the flame drops, indicating that the carbon has burnt out. The second stage ends when the vessel is turned down for a sample of the metal to be taken and the slag poured off. More lime is then added, and the blow is continued for a few seconds to complete the removal of the phosphorus; this forms the third stage.

First Stage.—The average duration of this was 12 minutes and 20 seconds. The blow begins with the expulsion of a large quantity of lime dust, and as soon as this has cleared away a flame is visible. It has a yellow or yellowish-red colour, the colour being probably caused by hydrocarbons from the tarry matter in the lining of the vessel. The flame grows larger and brighter, and assumes the usual appearance observed in the “acid” process. Sparks are thrown off, which in turn throw off other sparks; these are succeeded by larger showers of sparks and a louder roaring of the flame. When, after a time, the flame gets thin, some fume is seen; then the flame drops and the sparks do not throw off scintillations.

Second Stage.—This, technically known as the “over-blow,” lasts about $5\frac{1}{2}$ minutes. In the earlier part the flame is very short; it gradually extends, and the fume arises very copiously. It was noticed that the cloud of fume was yellower than that seen at Crewe and Dowlais in the “acid” process. On one occasion the fume was observed to have a rich purple colour when viewed by transmitted light, which colour faded gradually and became more like brown umber; the flame gradually increased in density until it became very brilliant indeed, but its colour was always of a golden-yellow, until sometimes it resembled phosphorus burning in oxygen. Slag is thrown out in large quantities, and with a shower of sparks, just prior to the converter being turned down.

Owing to the exigencies in the arrangement of the Bessemer plant and the nature of the operations carried on, it was found that the only point of observation available was a gallery at one end of a row of four converters, and when the most distant of these vessels was in use nearly all the details of the “blow” as photographed elsewhere in the “acid” process were absent.

For instance, the manganese bands were not defined or even clearly visible. Then again, the spectra were complicated by a superposed feeble solar spectrum. Only those vessels nearest the instrument yielded satisfactory photographs. It was proved eventually that the lime dust and other dust and smoke in the air reflected the sun’s rays and caused an overlying solar spectrum to appear. To get rid of this it became necessary to make all the observations during the evening after dark.

Having described the course of the “blow” in the Thomas-Gilchrist process, it will

be noticed that we have to observe the “blow” in different stages, and also the “over-blow”; it is desirable that some general account of the photographs which were taken at different times be recorded, and that the details of some of the spectra be given when of particular interest.

In all some twenty-six plates were developed, some few of which were failures owing to circumstances already described, but Nos. 4, 14, 15, 17, 23, and 26 were particularly valuable. A full account of all the details of the operations witnessed with a precise description of the spectra on each plate being considered unnecessary, the particulars of No. 14 only are here given, followed by a summary of all the spectra on the other plates. In making the observations it was found necessary at first for one person to attend to the spectrograph, a second to watch the “blow” and observe the flame with a direct-vision hand spectroscope, and obtain a record of what was taking place with the Anschütz camera, while the third recorded the time and entered the notes and remarks made to him. Subsequently, two observers were engaged—one in managing the spectrograph, the other in entering all details in the note-book. When a succession of thirteen spectra are photographed in 15 minutes, there is but little opportunity for entering notes of every detail. The omission of these details greatly diminishes the value of the observations; on the other hand, photographs of the operations greatly enhance their value.

Plate No. 14. A series of six spectra which are in very sharply defined focus in the green. The following table gives the intensities of the lines and bands in the different spectra from I. to VI., with the period of exposure in each case, the periods being consecutive.

Note.—There were 140 spectra on the twenty-six plates. The plates were numbered consecutively and the spectra on each plate were numbered in the order of their exposure. The references in the text to numbered plates relate to the *photographs* and not to illustrations, which have been omitted.

Wave-lengths.	Element.	Intensities numbered 1 to 10.						Description.
		I.	II.	III.	IV.	V.	VI.	
5893	Na	7	8	9	9	10	10	Centre of lines.
5832	FeK	—	—	—	1	2	2	Line and m.r.* edge of band.
5802	K	—	—	1	2	3	2	Sharp line.
5794	Fe	—	—	—	1	3	3	Sharp line.
5764	Mn	—	—	—	—	2	—	Sharp line.
5756	Mn	—	—	—	—	2	—	Sharp line.
5720	Mn	—	—	—	—	2	2	Broad line.
5690	Na	—	—	—	—	2	2	Line.
5609	Mn	—	—	—	—	—	—	Centre of dark space.
5582	Mn	1	2	4	8	8	7	m.r. edge of band.
5547	Ca	}	—	1	2	3	3	Weak lines which merge into a band.
5539	CaFe							
5439	Mn	—	—	2	3	4	3	Line on band.
5430	Mn	—	—	—	2	3	2	m.r. edge of band.
5408	Mn	—	—	—	—	1	—	Doubtful line.
5401	Mn	—	—	2	3	4	3	Line near edge of band.
5375	Mn	—	—	—	—	1	—	Doubtful line.
5364	Mn	—	1	2	3	4	3	m.r. edge of band.
5347	K	—	—	2	3	3	2	Line.
5331	K	—	—	—	—	1	—	Doubtful line.
5272	Mn	—	—	—	1	3	3	Line.
5242	Mn	—	—	—	1	3	2	Band.
5193	Mn	—	—	—	1	3	—	Line or edge of band.
5179	Mn	—	—	—	1	3	2	Edge of band.
5108	KFe	—	—	—	1	3	—	Line.
4644	K	—	—	1	3	3	1	Line.
4557	Cs	—	—	—	1	2	—	Line.
4485	Fe	—	—	—	—	2	3	Line.
4463	Fe	—	—	—	1	2	3	Line.
4429	Fe	—	—	—	1	3	3	Line.
4407	Fe	—	—	—	—	1	1	Line.
4385	Fe	—	—	—	—	1	2	Line.
4377	Fe	—	—	—	1	3	3	Line.
4227	Ca	—	—	1	3	4	3	Line.
4216	Rb	—	2	3	3	3	3	Line.
4202	Rb	1	3	5	5	5	4	Line.
4172	Ga	—	2	3	3	3	3	Line.
4048	K	}	6	7	8	9	9	7
4044	K							
4032	Mn	1	3	5	8	8	7	Middle of group.
Exposure periods . . .		m. s. 2 0	m. s. 2 0	m. s. 2 0	m. s. 2 2	m. s. 2 3	m. s. 0 54	

Intervals.—Between commencement of blowing and first exposure 3 minutes 35 seconds.

Between commencement of blowing and dropping of the flame 14 minutes 40 seconds.

Between first rising of fume from the over-blow and the end of the operation 4 minutes 25 seconds.

Duration of blow 22 minutes 35 seconds.

* m.r. = more refrangible.

The Cause of the Continuous Spectrum, which is a Marked Feature of the Flame from the "Basic" Process.

It has already been stated in the description of the "blow" as observed at the North-Eastern Steel Company's Works at Middlesbrough, that a flame is seen issuing from the mouth of the vessel from the first moment after the dispersion of the lime dust, a feature which is quite characteristic of the "basic" process. This flame is yellow and highly illuminating, but not to such an extent as to be visible on the slit plate of the instrument. It is evident, therefore, that some gas is evolved, the origin of which can only be the tarry matter used in the lining of the vessel. The smaller quantity of silicon in the iron is very quickly oxidised in this process. In the spectrum of the flame at this period it is observed that the continuous rays are generally stronger in the series of photographs taken at Middlesbrough than in those from Crewe and Dowlais, where the "acid" process was in use. This might be accounted for in part by the presence of larger quantities of the alkalis, which emit strong continuous flame spectra accompanied by lines, and partly by the presence of lime dust from the lime used in the "basic" process, which becomes incandescent in the flame. At this early period of the "blow" in the "acid" process only the lines of the alkali metals and of manganese appear, and they are very weak. The continuous spectrum cannot, however, be wholly attributed to the alkalis without further inquiry, for both iron and manganese or their compounds yield marked continuous spectra in the oxyhydrogen flame, which, however, is hotter than that of the flame of the converter at this stage. Moreover, in the "basic" as in the "acid" process, especially in the latter periods, this is caused by the flame of carbon monoxide. The visible spectra at Middlesbrough shortly after blowing has been started show the red and green bands of calcium oxide, and a minute later the lines of sodium. For instance, in the notes of our first series of photographs it is recorded that a flame was visible from the commencement, but it could not be seen upon the slit; there were showers of sparks and flashes of red at intervals during the first three minutes. The bands of manganese, two red lines, and the yellow sodium lines were visible. The manganese bands were mainly those in the violet. A subsequent examination of the photographs showed a band in the green due to calcium oxide, the lines of potassium 4047·36 and 4044·29, as also the manganese lines; hence one of the red lines belonged undoubtedly to calcium oxide, for this would certainly be present along with the green calcium oxide band; the other red line is more likely to be that of lithium than potassium, owing to the former being so much the brighter, and lithium we know by eye observations is always conspicuous in these spectra a few minutes before the potassium line appears. Lastly, we have the sodium rays in the yellow.

With reference to Plate 19, we have it recorded that the red and green bands of

calcium oxide were seen from the very first appearance of flame and for about two minutes of the "blow"; but the lithium and potassium lines appear rather more than a minute after the beginning. On Plate No. 17, which is a very complete series of thirteen photographs taken during a "blow" lasting 15 minutes, and commencing directly the converter was turned up, it was recorded that the red lines of lithium and potassium, with the yellow line of sodium, were plainly visible with the direct vision spectroscope as soon as the shower of lime dust cleared away after the "blow" commenced, that is to say, from the first appearance of the flame.

The bands of manganese were seen very early, but they were not sharp during the first 4 minutes; this refers to the bands in the green.

There can be no doubt that the immediate production of a flame is caused not by the oxidation of material in the bath, but by carbonaceous matter in the lining of the vessel; that its luminosity is due partly to the volatilisation of alkalis, but certainly, anterior to this effect, by the ignition of lime dust carried up by the blast into the flame.

Characteristics of the Spectra of the "Basic" Bessemer Flame.

A flame spectrum is observed shortly after the commencement of the "blow," consisting of a band of continuous rays of the red and green bands of calcium oxide. One minute later the red lines of lithium and potassium are seen with the lines of sodium. There are about fifty-three lines of iron as in the flame from the "acid" process, but the lines are of lesser intensity, and some of those near to, but more refrangible than, 4306.7 (the solar line G) are absent.

A number of lines which do not occur in the spectra of the flames from the "acid" process have been observed in most, if not all, of the spectra of the "basic" process. They have been traced partly to elements present in the lime, but the lines are chiefly caused by elements introduced with the iron, and are hitherto unrecognised constituents of the iron ores from which the crude metal is smelted for use in the Bessemer process. Rubidium and caesium undoubtedly accompany the lime, while as certainly gallium, copper, and silver, and some rubidium, enter with the iron. Lead lines were not observed in the flame, neither were nickel nor cobalt lines.

Another feature of these spectra is the less prominent appearance of the manganese bands, and lines of manganese, with the greater intensity of the lines of potassium.

The description of six spectra on Plate No. 14 (see p. 485) shows the increase in temperature of the flame with the progress of the "blow" until that period when the flame drops.

*The Identification of Lines and Bands observed in the Spectra of the Flames
from the "Basic" Process.*

In the region of the rays more refrangible than the strong manganese line λ 4030, no uncertainty is felt as to any line or band. The continuous spectrum extends throughout the whole of this portion to the edge of the plate, about λ 3210. It fades gradually, except at two places, from λ 3705 to 3600 and from λ 3581 to 3500, where two broad bands occur. These bands were observed in the Crewe Bessemer spectra, and in the spectra of manganese and its compounds heated in the oxyhydrogen flame (Flame Spectra), 'Phil. Trans.,' A, vol. 185, p. 1029. Between λ 4030 and 3448 the only lines detected are the iron lines, which are present without any considerable variation of intensity in the oxyhydrogen spectra of iron and its compounds. The lines just beyond λ 3448 are the pair of potassium lines, λ 3447·49 and 3446·49, the latter one slightly stronger than the former, and both of them stronger than the iron line 3440·7.

The iron line λ 3443·96 is present in some of the spectra. Between this point and the edge of the plate, about λ 3210, no iron lines are found either in the Middlesbrough or the oxyhydrogen spectra. Lines of other elements are visible on the photographs of several of the Middlesbrough spectra, the strongest being the sodium line λ 3303, which is really a pair of lines, but they are not distinctly separated unless the quantity of substance is very small. The silver line λ 3383·0 is present in several spectra, and on Plate 26 the second silver line λ 3280·8 is seen. On Plate 26 the second spectrum indicated by 26², in which the lines are very sharp near the edges of the plate, the two copper lines λ 3274·1 and 3247·7 are present, and beyond these again is the lithium line λ 3233 and the potassium line λ 3217·5. There is no indication of the spectrum of water vapour; the strongest lines in this spectrum would not, however, fall on the photographic plate used by us.

The identification of the lines and bands in the visible portion of the spectrum is much more difficult.

(1.) *Lines.*—Near the more refrangible end of the visible spectrum the manganese triplet occurs, each line being very strong; the neighbouring potassium lines λ 4044 and 4047 are also very strong. Next in order are four strong lines with wave-lengths 4171·5, 4201·9, 4216·0, and 4226·4.

These lines are not present in the Bessemer spectra from the "acid" process which we had hitherto examined, and their identification was not readily accomplished. The first fact noticed was that the first and last lines varied in strength independently of all other lines in the spectra, and that of the two intermediate lines, 4201·9 was always stronger than 4216·0. These two were, therefore, identified with rubidium, as they were the strongest lines in the oxyhydrogen flame spectrum of that element. The line 4226·4 was identified with calcium, this being decidedly the strongest line in

the oxyhydrogen flame spectrum of calcium oxide. It corresponds with a strong Fraunhofer line (best seen in Plate No. 4).

The oxyhydrogen spectrum of rubidium is such that no further lines of this element were expected, and none were found. In the case of the calcium oxide, the band in the green (the wave-length of its centre is about 5530) might be expected, and a band does occur, but this will be discussed later.

The line λ 4171.5 was identified only after a prolonged study. Of the many elements and compounds examined in the oxyhydrogen flame, none gave a strong line of this wave-length. Reference to published tables of arc and spark spectra indicated that it might be the strongest of the gallium lines.

LECOCQ DE BOISBAUDRAN gives the wave-length of the strongest of the lines of this element as 4170.4 on ÅNGSTRÖM'S scale, or 4171.0 on ROWLAND'S. The second line he gives as 4031.9 (ÅNGSTRÖM), 4032.6 (ROWLAND); this latter would lie between the two closely adjacent lines in the manganese triplet, and it would, therefore, be quite impossible to distinguish it when the manganese lines are so strong. No other strong lines are recorded, and this indication of the origin of the line could be confirmed only by analyses of the materials composing the lining of the converters, and of the "basic" earth and metals contained in the charge. By spectrographic analysis the same line was found in the oxyhydrogen spectrum of the crude iron ("mixer metal"). By chemical analysis the metals forming sesquioxides were freed from manganese, and the sesquioxides in this condition showed by spectrographic analysis the *two strong lines*, that with wave-length 4032.7 being weaker than 4171.5. The presence of gallium was proved by separating the pure oxide from a weighed quantity of metal, and determining the amount present. The purity of the oxide separated was established by spectrographic analysis ('Proc. Royal Society,' vol. 60, pp. 35 and 393).

Of the lines next in order, ten are identical with lines in the spectra of flames from the "acid" process and with lines in the oxyhydrogen flame spectrum of iron and its compounds. It must be remarked, however, that we now meet with notable differences in the *relative intensities* of these lines in the various Bessemer and oxyhydrogen flame spectra.

The differences, we believe, result wholly from differences in temperature, and our reasons for this we propose now to state.

The iron lines in this region of the spectrum of the oxyhydrogen flame appear on the following table, with varying intensities :—

VARIATIONS in the Intensity of Iron Lines in Spectra from various Sources.

Wave-lengths.		Intensity.									
Oxyhydrogen flame.	Identified in solar spectrum.	Solar.	Spark.	Arc.	Oxy-hydrogen flame.	CO + O flame.	Bessemer flame spectra.				
							Crewe.		Middlesbrough.		
							Temperature.		I.	II.	III.
							Low.	High.			
4063·75	4063·759	20	10	10	3	1	$\frac{1}{2}$	3	$\frac{1}{2}$
4071·92	4071·908	15	10	10	2	1	$\frac{1}{2}$	$2\frac{1}{2}$	$\frac{1}{2}$
4132·24	4132·235	10	8	10	1	...	$\frac{1}{2}$	1	$\frac{1}{2}$
4144·06	4144·038	15	7	10	1	...	$\frac{1}{2}$	$1\frac{1}{2}$	$\frac{1}{2}$
4202·20	4202·198	8	9	10	1	1	$\frac{1}{2}$
*4216·39	4216·351	3	2	6	1	$\frac{1}{2}$	2	4	$\frac{1}{2}$
4250·93	4250·945	8	8	10	1	$\frac{1}{2}$	$\frac{1}{2}$
4271·93	4271·934	15	10	10	4	2	1	4	$\frac{1}{2}$...	$\frac{1}{2}$
4308·06	4308·081	6	10	10	4	2	1	4	1	...	$\frac{1}{2}$
4325·94	4325·939	6	10	10	4	1	1	4	1	...	$\frac{1}{2}$
*4376·03	4376·107	6	4	8	2	2	3	5	4	2	3
4383·71	4383·720	15	10	10	8	4	3	6	4	1	3
4404·94	4404·927	10	10	10	$3\frac{1}{2}$	2	2	4	2	1	1
4415·29	4415·293	8	8	10	1	1	1
*4427·46	4427·482	5	3	8	2	2	3	5	5	2	$3\frac{1}{2}$
*4461·78	4461·818	4	3	6	1	1	$2\frac{1}{2}$	4	2	1	$2\frac{1}{2}$
*4482·34	4482·338	5	4	8	1	...	$1\frac{1}{2}$	3	1	1	1
*4489·86	4489·911	4	1	4	$\frac{1}{2}$	1	$\frac{1}{2}$

When the intensity is not stated in these columns the lines are either absent or exceedingly feeble, so that no value could be attached to them.

I. Plate 17, spectrum (8). II. Plate 14, spectra (5) and (6), and Plate 23 (2). III. Plate 26, spectrum (2).

A line at 4045 was hidden by overlying potassium lines. Two lines less refrangible than the above appear in seven of the Crewe spectra on Plate 8, and their intensity is 1.

The lines with wave-lengths 4215·0, 4375·19, 4426·7, 4461·5, and 4481·7 may all be classed as strong lines in the Bessemer flame spectra. In the spectrum of the flame during the earlier period of the blow they are practically the strongest lines of the above series. As the blow proceeds—that is to say, as the temperature increases—other lines, notably those with wave-lengths 4270·6, 4306·7, 4324·3, 4383·3 (this especially), and 4405·0, become stronger, while those just indicated are not strengthened in the same proportion.

The series of photographs taken at the Crewe works of the London and North-

* By interpolation. The other lines are coincident with strong lines in the spark spectrum.

Western Railway during the month of January, 1895, from which the details of two spectra are taken for comparison of the changes of intensity in the lines of iron, as given in the preceding table, show the gradual progress of these changes in a very marked degree. The solar spectrum lines are represented by ROWLAND'S figures for the comparative intensities, and lines of the other spectra are compared directly with these as photographed by us with the instrument which was used for the Bessemer spectra.

There can be but little doubt, if any, that the arc and solar spectra are more nearly alike in the intensity of their lines than any other two; next to the arc, we have the oxyhydrogen flame spectra and Bessemer spectra. The change in intensity is much more striking in the spark spectrum of iron. In this the lines of the first group are either absent or present only as very weak lines, while those of the second group are very strong lines.

We have clearly identified all the lines under discussion by making more accurate observations of the lines in the flame spectrum of iron. These latter measurements were made in the Chemical Laboratory of the University of Cambridge with a ROWLAND'S plane grating and spectrometer belonging to Professor LIVEING.

Oxide of iron heated in the carbon monoxide and oxygen flame gives a spectrum intermediate between the Bessemer and the oxyhydrogen flame spectra.

The next line beyond this group of iron lines is one of wave-length 4555.1. It is best seen on the third spectrum on the Plate 15 taken at Middlesbrough, but occurs also in other spectra. It is seen best in the earlier spectra of a blow, and is invisible in those which come later. It is, therefore, caused by a small quantity of a volatile element, unless, perhaps, the stronger continuous spectrum of the later periods of a blow masks the weaker lines. In this event, the weak lines of iron should also disappear, but they do not; so the first inference is probably correct. The strongest caesium line has, according to KAYSER and RUNGE, the wave-length 4555.44 in the arc spectrum, and the line in question is doubtless this line, which we know to be by far the strongest in the oxyhydrogen flame spectrum of caesium. Rubidium and other alkali metals are present, and the presence of caesium may therefore be expected.

On a New Line in the Spectrum of Potassium.

In many of the spectra a sharp line occurs near wave-length 4642. This line also becomes weaker, and on some plates disappears, during the later periods of the blow. It was not until after much careful study that it was finally traced to potassium. It is not recorded on any hitherto published arc, spark, or flame spectra of this element.

It occurs in the oxyhydrogen spectrum when potassium compounds are used, but it does not appear with the same intensity as in the Bessemer flame. Comparative

experiments were made in which, first, a very small quantity of the potassium compound was introduced into the oxyhydrogen flame; secondly, the potassium salt was volatilised in the oxygen and carbon monoxide flame. The line was of greater relative intensity in the latter spectrum, but it still did not equal that observed in the Bessemer flame.

There are two possible explanations of the reason for the disappearance of this line: first, its emissive power and its chemical action may be greater at lower temperatures, and, therefore, its photographic intensity greater; and, secondly, it may be that when the flame is less dense, so that the vapour pressure of the metal is decreased, the molecules are endowed with greater freedom of motion.

The following photographs were taken with the object of ascertaining whether the density of the vapour in the flame really affected the intensity of the line 4642:—

Plate 103, Spectrum (2).—Paper moistened with a solution containing 0·1 gramme of potassium chloride. Made into a coil, and burnt in the oxyhydrogen flame.

Spectrum (3).—The same as (2), but the paper was burnt in thin strips.

Spectrum (4).—Similar to (3), but 0·2 gramme of potassium chloride was present.

Plate 104, Spectrum (3).—Potassium chloride as in 103, Spectrum 3, but about one-half the quantity taken.

Spectrum (4).—Potassium chloride, about one-quarter of the quantity used for photographing Spectrum (3) on Plate 103. The vapour of potassium in the flame is known to be proportionally increased with the larger quantity of substance volatilised, and the intensity of the chemical action or emissive power of the continuous rays in these spectra is observed to be in the inverse proportion to the vapour pressure of the substance. With reduction of vapour pressure there is a diminution of chemical action exerted by continuous rays over a wide range of differences in wave-length, and this is accompanied by a greater intensity of chemical action or emissive power of the molecules for the ray λ 4642.

The question of the temperature was next examined, as up to this time the line had not been observed in a Bessemer flame.

Plate 373, Spectrum (1).—Spark spectra of metallic lines of known wave-lengths for measurements. Exposure, 30 seconds.

Spectra (2), (3), and (4).—Potassium chloride heated on a support of cyanite.

(2.) In the flame of hydrogen. Exposure, $1\frac{1}{4}$ hours.

(3.) In air and hydrogen, using the same burner as that for the oxyhydrogen flame.

Exposure, 15 minutes.

(4.) In the oxyhydrogen flame. Exposure, $1\frac{1}{2}$ minutes.

(5.) In the oxyhydrogen flame. Exposure, 5 minutes.

Two red lines were seen by using a small direct-vision spectroscop. These are doubtless the doublets $\left\{ \begin{matrix} 7699\cdot3 \\ 7665\cdot6 \end{matrix} \right\}$ and $\left\{ \begin{matrix} 6938\cdot8 \\ 6911\cdot2 \end{matrix} \right\}$, which have been observed in the arc spectrum of potassium.

The line 4642 was visible in all the above spectra. It was stronger in (2) than in (3), but strongest of all in (4).

The density of (5) was much greater than in any of the other photographs, but the intensity of the line was not proportionately increased, for there appeared to be very little difference between its intensity in Spectra (4) and (5).

Provided the temperature is sufficiently high to cause the emission of a ray with wave-length 4642, its brilliancy or intensity of chemical action is increased by diminishing the quantity of vapour or vapour-pressure in the flame, and thereby permitting the molecules so great a freedom of internal motion that it becomes possible for them to vibrate in the particular manner which causes the emission of this ray.

Taking a survey of all the plates upon which the line 4642 has been observed, and of those in which it is absent, and also having regard to the conditions under which the spectra in each case were produced, it is not so much reduction of temperature as reduction of quantity of vapour in the flame which increases its intensity.

The lines next in order are two of potassium with wave-lengths 5112 and 5098, which occur also in the oxyhydrogen flame, the arc, and spark spectra of potassium.

In the case of a line with wave-length 5112 it is probably intensified in some of the Bessemer flame spectra by a closely adjacent iron line, wave-length 5109, observed in the oxyhydrogen spectrum of iron.

About wave-length 5269 there is an iron line and at the more refrangible edge a manganese band. The iron line wave-length 5268.9 is the strongest in this region in the oxyhydrogen spectrum of iron.

At wave-length 5328 there is a line due in part each to iron and potassium; at λ 5343 a potassium line is seen, and at λ 5361 a line of potassium and the edge of a band of manganese.

In the earlier part of the blow a diffuse band occurs about 5540, and towards the end of the first part of the blow it appears to be replaced by two sharp lines. The change is best seen in the spectra on Plate No. 14. The band is due to calcium, but the lines are not calcium lines, for in the sixth spectrum on this plate the violet calcium line λ 4227 is much weaker than in the fifth spectrum, while the two lines are stronger.

The sixth spectrum is remarkable for an increase in the strength of the lines of iron throughout the whole spectrum, while the lines and bands of potassium and calcium are weaker. It is probable, therefore, that they are really iron lines. They are present in some Bessemer flame spectra photographed at Crewe in January, 1895, and occur in these only when the lines of iron are strongest. In the oxyhydrogen spectra of iron and its compounds the continuous spectrum is very strong in this region, but on very careful examination of a number of spectra we find a few in which traces of these two lines are present on the strong continuous spectrum. The relative intensity of the lines as compared with the other lines is, however, not equal to what obtains

in the Bessemer flame spectra. Failing to find corresponding lines in the spectrum of any other element, we have no hesitation, on the above evidence, in attributing them to iron. A line λ 5792 was identified in a similar way.

The line λ 5803 is a potassium line, which is seen as a strong line in the oxyhydrogen spectrum of potassium. The line λ 5833 is also present in the oxyhydrogen flame spectrum of potassium, and is, in some of the Bessemer flame spectra, intensified by an iron line, 5834.5, observed in oxyhydrogen flame spectra.

In the region of the spectrum just considered there are many bands, and these are almost wholly due to manganese or compounds of manganese. They coincide with bands in the oxyhydrogen flame spectra of manganese and its compounds; they are, in both series of spectra, all degraded towards the red, and the more refrangible edges are sharp. The measurement of the more refrangible edges only are given in the tables, and these measurements vary on different photographs as the intensities of the bands vary. Sometimes when there is a strong continuous spectrum present, the sharp edge of a band has the appearance of a broad or nebulous line. The three more refrangible bands terminate about wave-lengths 4561, 4402, and 4245, and near these positions there are lines in the Bessemer spectra which, according to their intensities, modify the appearance of the edges of the bands. The line near 4556 is the caesium line 4555, and in the other two cases, iron lines of wave-lengths 4404 and 4251.

Lines and Bands Less Refrangible than the D Lines.

We have been able to identify the lines and bands less refrangible than the D lines (which were photographed when using Lumière B plates) only by direct comparison with other spectra. We have no lines of reference on the Middlesbrough plates from which to draw a curve. A series of spectra was photographed at Crewe in January, 1895, on a plate stained with cyamine, and this includes both solar and Bessemer flame spectra. A curve of wave-lengths was drawn and the wave-lengths of the unknown lines and bands in the Bessemer flame spectrum were determined from it. By direct comparison of the Middlesbrough spectra with this plate, and by measurements of the oxyhydrogen flame spectra of the metals or compounds of lithium, manganese, and iron, we have identified the lines and bands in the Middlesbrough spectra. They were recorded in the analytical table of the second spectrum of Plate No. 26, and call for no special remark beyond the fact that the bands and lines are due chiefly to manganese, but are modified by bands and lines of iron, and possibly by the orange lithium line 6108.

The red lithium line 6708, and the red potassium lines 6938 and 6911, do not appear on the photographs, but were seen by the eye observations.

The Spectrum of the "Over-blow."

During the earlier part of the "over-blow" the flame is very short and not very luminous; the light emitted acts but feebly on a photographic plate. There is more fume expelled during this stage than during the first or carbon period of the "blow," and the quantity increases as the "over-blow" proceeds; the flame during this time increases in size and brilliancy, and towards the end emits a brilliant golden-yellow coloured light. There is a notable increase in the quantity of fume expelled after the "over-blow" has proceeded for 2 minutes.

The spectrum of the flame during these 2 minutes is very feeble, but during the latter $3\frac{1}{2}$ minutes it is much stronger. It extends from the red end of the spectrum to about wave-length 4000, in the violet; it is strongest in the green about wave-length 5500, but fades rapidly towards the violet.

The following lines have been observed in the photographs :—

Wave-length.

5893.	A line present in all the spectra, due to sodium.
5432.	Sharp, observed only on one plate, No. 16.
5394.	Sharp, observed on two plates, Nos. 16 and 17.
4047.	} Lines present in all spectra due to potassium.
4044.	
4034.	} Lines present in all spectra, due to manganese.
4033.	
4030.	

These lines are not as sharp on the photographs as the corresponding lines in the spectra photographed during the first period of the "blow."

The two lines, wave-lengths 5432 and 5394, coincide with two lines near the edges of the bands in the flame spectra of the manganese and its compounds. It was not apparent at first why these lines should be present in the spectra of some flames and not in the spectra of others, and they were not observed in the eye observations made during our first visit to Middlesbrough. In August, 1898, on a second visit to the same works, eye observations were made with the object of solving the problem. Three vessels, Nos. 2, 3, and 4, were in use on the day in question, and it was found that these two lines were strongest in the spectrum of the flame issuing during the "blow" from vessel No. 4, and also that the edge of the strongest green band was also seen.

The lines were sharp, and, when using a very narrow slit, stood out clearly on the strong continuous spectrum. The two lines were stronger in the spectrum of the flame issuing from No. 3 vessel than in that from No. 2 vessel. They were observed in two or three "blows" in each vessel and with similar results each time.

It was found from the inquiries made of the officials that whilst all three vessels were receiving similar charges of metal and lime, the lining of vessel No. 4 was almost new, and a new bottom had been fitted to it shortly before the time of observation. About forty charges had been blown in vessel No. 3, and about seventy in No. 2. The intensity of the line diminishes therefore with the age of the lining.

The tar in the lining is not wholly decomposed when the lining is worn out, but the rate of the decomposition and the quantity of the volatile products must be less than in a new lining, and it appears to us that it is the volatile products of the decomposing tar which cause these lines to appear in the spectra of the flames. In the "acid" process the flame drops as soon as the carbon is oxidised; the bands and lines in the spectrum immediately become diffuse, and the spectrum presents more the appearance of a continuous band of rays. According to Sir I. LOWTHIAN BELL, carbon monoxide is much more stable in presence of iron at high temperatures than carbon dioxide. SNELUS ('Chem. News,' vol. 24, p. 159) has shown that the proportion of the former oxide exceeds that of the latter in the gases issuing from the converter in the "acid" process during the latter two-thirds of the time, and towards the end there is no carbon dioxide present; so that all the carbon in the volatile products from the tar will exist in the flame during the "over-blow" as carbon monoxide. The hydrogen in these products and in the water vapour in the blast will pass out of the converter in the elementary state. These reducing gases acting on the compounds of manganese in the slag reduce some of the metal, which then passes off as vapour. The combustion of the hot gases, carbon monoxide, and hydrogen outside the vessel will give a hotter flame, and the increased temperature, together with the reducing gases in the flame, will account for the increased intensity of the manganese spectrum.

There are two points regarding the flame of the "over-blow" which require explanation. First, the great brilliancy of the flame during the latter part of the blow; secondly, the absence of the spectra of iron and calcium, and the feeble character of the spectra of potassium, sodium, and manganese.

Immediately the carbon is burnt out of the iron the flame drops to about one-sixth of its height; its luminosity also diminishes, and the quantity of fume increases. There can be no considerable variation in the temperature of the fluid charge during the few moments in which this great change takes place; the gases will therefore leave the converter at about the same temperature throughout this time.

It is probable that the impurities in the iron are oxidised chiefly by secondary reactions, but a portion of them is oxidised directly by the oxygen of the air. The volume of the iron in the converter is very much greater than the volume of the manganese, and yet almost the whole of the latter is oxidised and passes into the slag in the first few minutes of the "blow." The fact that the flame maintains its size until the sudden drop confirms this hypothesis. If this hypothesis is true the

greater portion of the oxygen of the air enters into combination with iron, forming magnetic oxide of iron which is probably reduced to a lower oxide. This oxide of iron will be reduced to the metal by the silicon, manganese, and carbon present in the iron, and by the phosphorus or ferrous phosphide in presence of the lime in the order stated, and if the time of oxidation were extended indefinitely each one would be oxidised almost completely in turn. In the converter the oxidation is so rapid that all the reactions go on together; but the complete oxidation of each impurity is achieved in the order named.

Any phosphorus oxidised in the early part of the "blow" in contact with and entering into combination with the lime is finally removed from the iron, as the resulting compound is not reduced by the reducing agents present. About one-half the phosphorus is oxidised in this way before the flame drops ('J. I. and S. Inst.,' 1896, No. 1, p. 465).

The chief cause of the flame in the "acid" process has been shown to be carbon monoxide which, leaving the vessel at a high temperature, accompanied by vapours of iron, manganese, &c., is burnt by the oxygen of the air. The hottest part of this flame is the outer layer, where the temperature is increased by the combustion of the carbon monoxide and hydrogen. When the carbon is completely removed from the iron in the "basic" process, there is still the appearance of a flame which increases in length as the "over-blow" proceeds; the quantity of fume expelled increases rapidly at this period also. The short flame is bright, and may consist principally of finely divided particles of oxide of iron heated to the temperature of the bath of metal and slag, and by the heat evolved by the combustion of metallic vapour inside the vessel. The particles of matter expelled from the vessel are of two kinds: one consists of larger particles of slag produced by the violent agitation of the fluid charge inside the converter; these quickly fall to the ground. The other kind is the fume proper, composed of the products of combustion of the metallic vapours. The particles forming this fume are undoubtedly very small; this is proved by the fact that they scatter the light falling on them, and cast* a brown shadow, and also by the great height to which the cloud ascends. These very small particles will be kept at the temperature of the escaping gases.

The spectrum during the "over-blow" is very feeble in the violet and does not extend beyond 4000. The spectrum of the lime-light extends into the ultra-violet, so also does the light emitted mainly from the furnace walls, through the working doors of a Siemens-Martin steel-melting furnace.

It appears, therefore, that the temperature of the source of light in the flame of the "over-blow" is comparatively low, approaching that of a yellowish-white heat, and that the light of what is apparently a flame emanates from a torrent of very small particles, liquid or solid, heated to a temperature of such luminosity.

* Mr. C. H. RIDSDALE first remarked the colour of this shadow (see 'Journ. Iron and Steel Institute,' No. 2, 1895, p. 35).

The temperature of the flame of the "over-blow" is therefore much lower than during the first period, when highly heated carbon monoxide is undergoing combustion. This will, at least in part, account for the feeble character of the line spectra of the alkalis, &c., at this stage. Another reason for this is discovered in the work of GOUY ('C. R.,' vol. 83, pp. 70-2; 'Phil. Mag.,' 1877, No. 2, p. 156), who found that with salts of lithium, calcium, strontium, and barium the maximum intensity of their flame spectra is reached "before the flame ceases to be reducing (for a copper wire), and is followed by a rapid diminution. With a large excess of air the spectrum disappears." The facts appear unfavourable to the opinion which attributes the bands of their spectra to oxides. "With sodium, on the contrary, the brightness of the flame augments rapidly as it becomes less reducing; the maximum is produced at the instant it ceases to be so, and is followed by a reduction of brightness much slower than with other metals."

Now without the decomposition products of the tar in the lining of the converter the flame cannot be more than feebly reducing; the only reducing gas is the hydrogen resulting from the decomposition of the water vapour in the air. GOUY'S results, therefore, also in part explain the absence of the line and bands of calcium, and account for the feeble character of the other lines and for the changes in the spectrum described below.* The quantity of fume expelled is very great in the latter part of the "over-blow"; it is mainly composed of oxide of iron, and yet no bands nor lines of iron are present in the spectrum.

The brilliancy of the flame is so great towards the end of the "blow" that we were led to suppose that it might be due in part to an oxide of phosphorus. It is practically impossible to collect a sample of the fume free from the slag, and hence no direct evidence can be obtained on this point. F. E. THOMPSON states ('J. I. and S. Inst.,' 1896, No. 1, p. 464) that "phosphorus towards the end of 'hot blows' does not pass readily into the slag, and scrap must be added," that is, to cool the bath. This indicates that at the highest temperatures, in presence of a large excess of molten iron, phosphorus pentoxide is not formed as readily as at lower temperatures; the less acid lower oxide of phosphorus would probably pass away with the nitrogen and be converted into phosphorus pentoxide by the external air.

* In the blow recorded on Plate 17 the red lines of the lithium and potassium with the yellow lines of sodium were seen with the direct-vision spectroscope as soon as the vessel was turned up. The bands of manganese appeared very early, but they were not sharp during the first four minutes; they increased in brilliancy throughout the first part of the blow, that is to say, until the flame dropped. The lithium and potassium lines continued very bright throughout the whole of this period. At the dropping of the flame the bands all disappeared, as practically also did the lithium and potassium lines, the yellow sodium lines alone remaining visible in the weak continuous spectrum. The flame at this time was very short and feeble. It lengthened slowly as the blow proceeded, until it became about one-fourth to one-third the length of the longest flame of the first period, and the lithium and potassium lines became stronger. When the fume began to issue in quantity it had at first a rich purple colour by transmitted light, which colour faded gradually, then became like brown amber, while the flame turned denser and denser until before long it had become very brilliant indeed. The appearance during the "after-blow" (third period) was similar to that at the end of the second period.

LINES and Bands observed in the Spectra of "Basic" Bessemer Flames and the Lines and Bands in Oxyhydrogen Flame Spectra with which they have been identified.

Wave-lengths.	Element.	Oxyhydrogen flame spectra.	
		Wave-length.	Description.
6290	Fe	6290·0	Beginning of a band.
6240	Mn	6240·0	Broad line.
6236	Fe	6236·0	m.r. edge of band.
6211	Mn	6211·0	Broad line.
6182	Mn	6182·0	"
6160	Mn	6160·0	"
6103	Fe	6103·0	Line.
	Li	6104·0	"
6092	Fe	6092·0	"
5972	Mn	5972·0	Line or edge of band.
	Fe	5981·0	Line.
5945	Mn	5945·0	Line or edge of band.
	Fe	5940·0	Line.
5893	Na	5893·2	Middle of D. and D.
5864	Mn	5854·0	m.r. edge of band.
	Fe	5870·0	" "
5833	K	5834·5	Line.
	Fe	5831·7	"
5803	K	5799·6	Strong line.
5793	Fe	5789·8	Line.
5764	Mn	5765·6	Line on band.
5756	Mn	5753·8	" "
5720	Mn	5716·5	" "
5690	Na	5686·0	Broad line on band.
5614	Mn	5612·0	Middle of broad line on band.
5581	Mn	5583·7	m.r. edge of very strong band.
5547	Ca	5543·5	(Eder and Valenta line.)
5520	Ca	5517·0	" " "
5439	Mn	5434·7	Line on band.
5430	Mn	5432·2	" "
5408 ?	Fe	5403·2	Weak line.
5401	Mn	5394·0	Middle of line on band.
5387	Mn	5390·5	" " "
5361	Mn	5359·5	m.r. edge of band.
	K	5360·0	Strong line.
5343	K	5340·2	" "
5328	K	5324·0	Weak line.
	Fe	5326·9	Line.
5269	Mn	5266·5	m.r. edge of band.
	Fe	5268·9	Line.
5232	Mn	5230·0	m.r. edge of band.
5193	Mn	5192·0	" "
5161	Mn	5158·0	" "
5110	K	5111·4	Weak line.
	Fe	5109·0	Very weak line.
5097	K	5098·4	Weak line.
5090	Mn	5090·4	m.r. edge of band.
5052	Mn	5051·0	" "
5017	Mn	5012·5	" "
	Fe	5010·5	Very weak line.
4980	Mn	4978·2	m.r. edge of band.

Lines and Bands observed in the Spectra of "Basic" Bessemer Flames and the Lines and Bands in Oxyhydrogen Flame Spectra with which they have been identified—*continued.*

Wave-lengths.	Element.	Oxyhydrogen flame spectra.	
		Wave-length.	Description.
4935	Mn	4933·2	m.r. edge of band.
4890	Mn	4894·0	" "
4853	Mn	4854·5	" "
4820	Mn	4825·0	Line.
4786	Mn	4784·5	"
4735	Mn	4739·0	m.r. edge of band.
4643	K	4642·4	Line.
4556	Cs	4555·4	Very strong line.
	Mn	4561·3	m.r. edge of band.
4483	Fe	4482·34	Very weak line.
4463	Fe	4461·78	" "
4428	Fe	4427·46	" "
4406	Fe	4404·94	Weak line.
	Mn	4402·2	m.r. edge of band.
4384	Fe	4383·71	Line.
4377	Fe	4376·03	Weak line.
4327	Fe	4325·94	" "
4307	Fe	4308·06	" "
4272	Fe	4271·93	" "
4250	Fe	4250·93	Very weak line.
	Mn	4245·4	m.r. edge of band.
4227	Ca	4226·93	Very strong line.
4217	Rb	4215·9	Strong line.
	Fe	4216·39	Weak line.
4202	Rb	4202·0	Very strong line.
	Fe	4202·20	Weak line.
4172	Ga	4171·6	Very strong line.
	Fe	4144·06	Weak line.
	Fe	4132·24	" "
In Spectrum.			
26 ²	Fe	4071·92	Weak line.
"	Fe	4063·75	" "
4047·4	K	4047·4	Strong line.
	Fe	4058·8	Line.
4043·8	K	4044·0	Very strong line.
4034·0	Mn	4034·5	" "
4033·1	Mn	4033·2	" "
4030·5	Mn	4031·0	" "
3929·6	Fe	3930·5	Strong line.
3927·4	Fe	3928·0	" "
3923·3	Fe	3922·8	" "
3920·7	Fe	3920·0	" "
3907·5	Fe	3906·4	Weak line.
3899·5	Fe	3899·9	Strong line.
3895·5	Fe	3895·9	" "
3886·4	Fe	3886·2	Very strong line.
3878·7	Fe	3878·9	" "
3860·0	Fe	3860·1	" "
3856·3	Fe	3856·6	" "

Lines and Bands observed in the Spectra of "Basic" Bessemer Flames and the Lines and Bands in Oxyhydrogen Flame Spectra with which they have been identified—*continued.*

Wave-lengths.	Element.	Oxyhydrogen flame spectra.	
		Wave-length.	Description.
3840·0	Fe	3840·2	Weak line.
3833·7	Fe	3834·2	" "
3825·4	Fe	3825·9	Line.
3824·1	Fe	3824·5	Very strong line.
3820·7	Fe	3820·6	" "
3766·7	Fe	3767·2	Weak line.
3763·5	Fe	3763·8	" "
3758·6	Fe	3758·4	Line.
3749·4	Fe	3749·3	Very strong line.
3748·6	Fe	3748·2	" "
3746·0	Fe	3745·8	" "
3737·4	Fe	3737·4	Very strong line.
3735·2	Fe	3735·1	Strong line.
3733·7	Fe	3733·3	Line.
3726·0	Fe	3727·9	Very weak line.
3722·8	Fe	3722·5	Strong line.
3720·1	Fe	3719·9	Very strong line.
3706·0	Fe	3705·7	" "
3680·0	Fe	3679·9	Strong line.
3648·0	Fe	3647·8	Weak line.
3633·0	Fe	3631·2	" "
3619·0	Fe	3618·7	" "
3609·0	Fe	3609·0	" "
3581·5	Fe	3581·5	Strong line.
3570·1	Fe	3570·1	Weak line.
3566·0	Fe	3565·5	" "
3526·0	Fe	3525·9	" "
3523·0	Fe	3521·2	Very weak line.
3498·0	Fe	3497·6	Weak line.
3491·0	Fe	3490·7	Line.
3477·0	Fe	3476·6	Very weak line.
3475·5	Fe	3475·4	Line.
3466·0	Fe	3466·0	" "
3447·0	K	3447·5	Strong line.
3446·0	K	3446·4	" "
3445·0	Fe	3443·8	Very weak line.
3441·0	Fe	3440·7	Very strong line.
3382·0	Ag	3383·0	" "
3303·0	Na	3303·0	Strong line
		3302·5	" " } a doublet.
3283·0	Ag	3281·0	Very strong line.
3275·0	Cu	3274·0	" "
3247·0	Cu	3247·7	" "
3228·0	Li	3233·0	Strong line.
3221·0	K	3217·0	" "

In order to confirm the results obtained by observations made on the flame from the converters, we decided to examine the metal with which the vessels are charged.

A tabulated statement of the spectrographic analysis of the metal is published in the 'Transactions of the Chemical Society,' vol. 79, p. 61, 1901. An account of the chemical analysis and the separation of the different constituent substances has already been communicated to the Society ('Proc. Roy. Soc.,' vol. 60, p. 393).

Analysis of the Crude Metal and Raw Materials used in the Manufacture of Steel.

The mixture of raw iron from the blast furnaces with molten pig iron from a cupola, and technically termed "mixer metal," was submitted to spectrographic analysis. The identity of such lines as were due to the presence of foreign metals was proved by carefully executed chemical analyses and by measurements from the photographs of the spectra of the various precipitated substances which were separated from the iron.

Mr. C. H. RIDSDALE very kindly supplied us with samples of the following raw materials:—

Roasted Cleveland ore, manganese ore, tap cinder, mixer metal, and burnt lime. Also a sample of flue dust from a blast furnace plant and a sample of the old lining of a converter.

These were analysed by heating each of them on a cyanite support in the oxyhydrogen flame for about half an hour, and photographing the spectrum of the flame coloured by the vapours of substances volatilised from them. The results are as follows:—

Roasted Cleveland ore contains iron, sodium, potassium, manganese, chromium, copper, gallium, lead, calcium.

Manganese ore contains manganese, iron, sodium, potassium, silver, copper, lead, indium, and calcium.

Tap cinder contains iron, sodium, potassium, manganese, copper, and lead.

Mixer metal contains, besides iron, sodium, potassium, nickel, copper, chromium, gallium, and manganese; also lead, cobalt, and silver in smaller proportions.

Burnt lime contains calcium, strontium, manganese, magnesium, iron, potassium, and sodium.

Flue dust contains iron, sodium, potassium, nickel, copper, silver, chromium, gallium, lead, manganese, calcium, and rubidium.

Old converter lining contains calcium, magnesium, iron, potassium, sodium, and strontium.

Some analyses have been made on larger quantities of materials, and the presence of some other elements detected. Rubidium, strontium, and magnesium occur in the part of the Cleveland ore which is insoluble in hydrochloric acid. Rubidium also occurs in the manganese ore.

The tap cinder contains traces of gallium and chromium. It is well known that

vanadium is present both in the Cleveland ore, in the iron smelted from it, and in the basic slag. The basic Bessemer steel appears to be free from vanadium. This element gives no spectrum in the oxyhydrogen flame by which its presence may be recognised, but we have detected it by chemical reactions in solutions of the iron and of the basic slag.

The oxyhydrogen flame spectra of all the elements named above have been studied in the course of this investigation, as well as those of nearly all of the other elements.

The basic steel contains the following elements: Iron, gallium, manganese, lead, copper, nickel, cobalt, silver, chromium, calcium, sodium, and potassium. The chromium, cobalt, and silver are present in minute traces.

The Bessemer flame spectrum does not contain any lines of strontium, chromium, nickel, cobalt, or lead, elements present in the raw materials which are easily recognised by lines in the oxyhydrogen flame spectra. These are doubtless present in too small quantities to give lines strong enough to appear on the strong continuous spectrum; some of the weaker iron lines are also lost in the continuous spectrum in many of the Bessemer flame spectra photographed.

Some attempts were made to reproduce the more complex part of the spectrum of the Bessemer flame in the laboratory. Rolls of filter paper containing a powdered mixture of compounds of iron, manganese, potassium, sodium, and calcium were burnt in the oxyhydrogen flame, and the spectrum photographed in the same instrument as was used at Middlesbrough. After a few experiments, in which different proportions of the constituents were used, a mixture was arrived at which gave a very fair copy of the Bessemer flame spectrum.

Conclusions.

- (1.) *Line spectra are not observed in the open-hearth furnace.*

The open-hearth furnace, though at a temperature as high as that of the Bessemer converter, does not show in a photograph the spectra of any of the metals known to be present, but a band of continuous rays extending from the red into the ultra-violet. The reason is that the atmosphere of the furnace is an oxidising one, and, moreover, the oxidation becomes greater when the furnace doors are opened. This was shown by observations on a cupola furnace; the metallic lines were visible only when the blast was turned off, that is to say, when the atmosphere had a reducing action.

- (2.) *The phenomena of the "basic" Bessemer blow differ considerably from those of the "acid" process.*

First, from the very commencement of blowing a luminous flame appears. It is visible as soon as the lime dust has been blown out of the vessel. We have proved that it might proceed from possibly three sources: ignited lime dust, ignited alkali metals, which give a continuous spectrum, and hydrocarbons from the tar mixed with

the "basic" lining of the vessel. Such ignition could only take place at this stage in consequence of the combustion of highly heated carbon monoxide or a hydrocarbon, and the presence of this latter substance is easily accounted for.

We conclude that the immediate production of a flame is caused not by the oxidation of material in the bath of metal, but by carbonaceous matter in the lining of the converter; that its luminosity is due partly to the volatilisation of the alkalis or alkali metals, but certainly prior to this effect to the incandescence of a cloud of lime dust carried up by the blast into the flame.

Secondly, volatilisation of metals occurs largely at an early period in the blow, and is due to the difference in the composition of the metal blown. In the "acid" process the crude metal contains much silicon, carbon, and manganese. The combination of the silicon and manganese with oxygen is the cause of the high temperature attained without any indication of the flame which subsequently appears, for both the products of combustion of silicon and manganese are liquid slags at that high temperature. In the "basic" process the combustion of carbon takes place at a much earlier period, because there is practically no distinct period when siliceous slags are formed; with the carbon monoxide the metals are volatilised, the atmosphere being a reducing one.

Thirdly, a very large amount of fume is formed at the close of the second period. This arises from the oxidation of metal and of phosphorus in the iron phosphide being productive of a high temperature, but little or no carbon remaining in the bath; the flame is comparatively short, and the metallic vapours carried up are burnt by the blast.

Fourthly, the over-blow is characterised by a very powerful illumination, from what appears to be a brilliant yellow flame which is generated within the vessel. During this over-blow there is a copious production of dense fume, composed of oxidised metallic vapours, chiefly iron. The particles forming the fume are undoubtedly of very minute dimensions, as is proved by the fact that they scatter the light which falls upon them and cast a brown shadow, and the cloud of fume ascends to a great height before it is dispersed. Such small particles while within the vessel are, doubtless, at the same temperature as the escaping gases. The spectrum of the over-blow is continuous and very feeble in the ultra-violet, as it does not extend beyond wave-length 4000. This indicates that the source of light is at a comparatively low temperature, approaching that of a yellowish-white heat. We conclude, therefore, that the source of light, or what apparently is a flame, really emanates from a torrent of very small particles, liquid or solid, at a yellowish-white heat. From the spectrum measurements we have evidence that the source of light during the over-blow is at a much lower temperature than that which prevails during the first period, when the highly heated carbon monoxide is undergoing combustion. This is sufficient to account for the feeble character of the line spectra of the alkali metals, &c., seen at this stage in the band of continuous rays. But a second reason for this

may be found in the observation of GOUY, that a large excess of air causes the spectra of lithium, calcium, strontium, and barium salts to disappear, and the maximum intensity of their flame spectra is attained before the flame ceases to exert a reducing action. The spectrum of sodium is not affected in the same way, but, on the contrary, the intensity of its emitted rays increases rapidly as the flame diminishes in reducing power, and is at its maximum at the instant it ceases to be a reducing flame. The subsequent reduction in brightness is much slower than with the other metals. We believe, therefore, that GOUY'S results, in part, offer a satisfactory explanation of the absence of the lines and bands of calcium, and account for the feeble character of the other lines and for the changes in the spectrum already described (see pp. 485 and 498).

Fifthly, the spectra of flames from the "basic" process differ from those of the "acid" process in this respect that the manganese bands are almost entirely absent, but lines of elements not usually associated with Bessemer metal, and which have not appeared in previous photographs, are seen in these. We have proved that the difference in the spectra is due in the first place to a difference in the composition of the crude blast-furnace iron, which is best adapted to the working of the basic process. A second reason is the use of charges of "basic" materials placed in the vessel with the metal. The potassium, sodium, lithium, rubidium, and caesium have been traced to the lime; the manganese, copper, silver, and gallium to the ore.

Other constituents, such as vanadium and titanium, are not in evidence, because they do not yield flame spectra, and, furthermore, because they pass in an oxidised state along with the phosphorus into the "basic" cinder.

(3.) *Differences in the Intensity of Metallic Lines.*

Iron lines to the number of fifty-three have been measured, as in the spectra of flames from the "acid" process, but they are of lower intensity, and some of those near the position of the solar line G are absent.

There is a less prominent appearance of the manganese lines and bands, the cause of which has already been stated; but there is a greater intensity of the lines of potassium and calcium, and to these the elements—rubidium, caesium, gallium, copper, and silver, must be added.

The variations in intensity of the iron lines in the "basic" Bessemer flame are due to differences in temperature solely.

There are two lines which in some spectra appear to have become intensified, while the calcium band wave-length about 5540 has become greatly enfeebled. It seemed as if they had arisen out of the calcium band, but they are not calcium lines.

They have been observed in many different spectra of Bessemer flames and of iron and its compounds in the oxyhydrogen flame, and they are strongest where the iron lines are strongest. As no corresponding lines have been found in the spectrum of any other element, we believe we are justified in attributing them to iron.

Another line, 5792, was identified with iron in a similar manner.

Lines of potassium and the edges of manganese bands are shown to have been intensified by the proximity of iron lines in some cases. The following are examples : λ 5864, Fe λ 5870, Mn band 5269, Fe λ 5268·9. The line λ 5361 is common to both potassium and manganese, and 5343 to potassium and iron. A similar case has already been observed by us with two rubidium lines, 4216·3 and 4203·2, and two iron lines.

(4.) *A New Line of Potassium with Variable Intensity.*

The new line in the spectrum of potassium, wave-length approximately 4642, varies in intensity or disappears altogether; but provided the temperature is sufficiently high to cause the element to emit this ray, its brilliancy or intensity of chemical action is increased by diminishing the quantity of vapour in the flame, and so giving greater freedom of motion to the molecules. From a minute examination of all the plates on which the line 4642 has been photographed, and of those in which it is absent, and also having regard to the conditions under which the spectra in each case were produced, we conclude that it is not so much reduction of temperature, as reduction of the quantity of vapour in the flame, which increases its intensity.

This much is quite certain, that increase of intensity does not in this instance indicate a higher temperature.

We desire to record our sincere thanks for permission and facilities given to us to visit the works for the purpose of carrying out these researches, first to Mr. ARTHUR COOPER, Managing Director of the North-Eastern Steel Company, and to Mr. F. W. WEBB, Chief Engineer of the Locomotive Department of the London and North-Western Railway; for assistance cordially rendered by Mr. C. H. RIDSDALE, the chemist to the North-Eastern Steel Company, and by our friend Mr. E. V. CLARK, A.R.S.M., sometime Demonstrator of Chemistry and Assaying in the Royal College of Science, Dublin.

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