

PYRITIC SMELTING OF A NICKEL-COPPER SULPHIDE ORE.

Contractor

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and

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1910.

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INTRODUCTION.

The subject of this thesis ia pyritic smelting in the Institute blast furnace of a mixture of copper-nickel matte and cupriferous pyrite. With the ordinary reducing smelting in the Institute blast furnace, 18% of coke is used which furnishes a reducing atmosphere. In pyritic smelting, no coke or only a small amount 1s used, and this causes the smelting to taka place under oxidizing conditions. The oxidation of the iron and sulphar of the sulphide of iron and the formation of the slag, furnish the whole or the greater part of the heat necessary. For the success nf tha process, it is necessary to have an abundant supply of air at the right pressure and a sufficient quantity of silica to slag off the iron which 13 not required for the desired grade of matte. The matte concentration is affected by the amount of air furnished, by the quantity of silicia present and by the coke added.The slag composition under given conditions is always constant. An increasa of silica will not change this composition, but causes the formation of a larger quantity of slag and a rise in the grade of the mette. \backslash

MATERIALS.

The ore smelted consisted of equal parts of coppernickel matte and cupriferous pyrite.

Matte. The matte used was a mixture of four lots of coppsr matte and one lot of nickel matte produced at the Institute in laborax tory runs and in a thesis run of 1908. The five lots of matte

were separately broken by hand to 30 mm. and screwed on 8 mm. sieve to remove the fines, as only the oversize was to be used. This was sampled by fractional S91sction, one tenth part by weight of each lot being reserved as sample. The samples were combined and reduced to $1/4$ inch in the Sturtevant roll-jaw . crusher. The combined sample was then halved in the Jones samplar and the reserved portion put through the Hendrlck-Bolthoff sample grinder to pass a 30 mesh sieve, then split-shoveled down to 485 grams and this ground on the bucking plate to pass a *t,* 100 mesh screen. The matte was found to be magnetic, hence the metallic iron particles from the machines could not be removed with a magnet.

The matte was analyzed for $Cu, N1, Fe, Pb, S, CaO,$ $\mathbf{A1}_{2}^{\circ}$ O₃ and S10₂

The sample for analysis was treated with a solution of bromide in $HNO₃$ (Sp.Gr.1.42). After action ceased, concentrated HO/was added, and the SOlution boiled until no more substance was dissolved. The residue was then filtered, fused with Na₂ CO₃and added to the main solution. The solution was then evaporated to dryness, dehydrated, H0/and water were added, and the silica filtered off, washed, ignited, and weighed.

 x Foot-note from 1st. page:-- Thesis No. 341 by A. H. Bradford and C. A. Gibbons, Jr.

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H2 S was passed into the slightly acid filtrate, the sulphides of copper and lead were precipitated and filtered. The precipitate was dissolved in H N O₃ and the solution electrolyzed. The copper was weighed as Cu and the lead as PbO.,

The filtrate was evaporated nearly to dryness with H_2 S O_4 water was added, and the solution passed through a Jones reductor. The iron was determined by titrating with K MnO_A After titrating the solution was eveporated to about 250 $\dot{\mathsf{q}}$., and the nickel precipitated by the dimethylglyoxime method and weighed as $C_g H_{14} N_4 O_4 N_1$.

A fresh sample was taken for the determination of CaO and Al $_2$ O₃. It was put into solution as above, SiO₂, Cu and Pb were separated as shown, and the combined hydroxides of aluminum and iron thrown down by means of a double ammonia precipitation, filtered, ignited and weighed. As some nickel is carried down its amount has to be determined. This was done by fusing the ignited precipitate with $KHSO_A$, taking up with water, precipitating with dimethylglyoxime, and weighing. Deducting the weight of the previously determined oxides of iron and nickel gave the $A1_2$ 0_3 .

The calcium was precipitated in the filtrate as calcium oxalate.The precipitate was dissolved in H $_{2}$ SO₄ and titrated hot with \texttt{KMnO}_A .

Sulphur was determined in one sample by the Fresenius method of fusing with Na₂ CO₃and K N O₃ and in another by the Glaser method of fusing with $Najoj$

The matte was found to contain some magnetic oxide of iron. The analysis gave the following results:

0 as FeO and Fe₃O₄.

Pyrite. The pyrite used came from the Eustis mine at Capleton, Province of Quebec, Canada. The ore was a massive copperbearing pyrite with some quartz as gangue. It was broken by hand to pass a 30 mm. screen, the smalls, finer than 8 mm. were removed by screening. The coarse ore was halved by fractional selection and one half sampled by taking pieces from it when spread on the flcor. The sample was crushed in the Sturtevant rOll-Jaw crusher, cut in half by means of the Jones sampler and ground in the Hendrick τ Bclthoff sample grinder. The pulp was then split-shoveled to 210 grams and this amount bucked through a 100-mesh sieve. The metallic iron from the wear of the machines was removed with a magnet.

The pyrite was analyzed for $S10₂$, $F₀$, $A1₀03$. S, and α , The SiO , combined oxides of iron and aluminum and S 2 were determined in one sample, as followd:

A sample of about $5/10$ gram. ef pyrite was dissolved in 20 c.c. of a frahly-made mixture of three volumes HNO_3 $(Sp, gr.1.42)$ and one volume of HCl (Sp. gr. 1.20). When disintegration was complete 5c.c. of sodium carbonate solution wers added. The whole was evaporated to dryness,treated with 50.c. Hel and dehydrated. The residue wae moistened with

le.c. HCl, 100 c.c. of hot water were added, the whole heated to boiling and the silica filtered off, washed, and ignited and weighed. A test with HF showed that the insoluble residue was silica.

The filtrate was treated with bromine water to oxidize the iron. The combined oxides of iron and aluminum were precipitated by pouring the hot filtrate into an excess of ammonia, filtering off the hydroxides. They were re-dissolvedin HCl and re-precipitated with ammonia. This second filtrate and the washing were added to the first filtrate. The precipitate was ignited and weighed as Fe_2O_3 and $A1_2O_3$ Sulphur was determined as Ba ${so}_{4}$ by precipitating with Ba ${cs}_{2}$ in the hot filtrate.

Iron was determined from the second sample of pyrite by dissolving in the same mixture of nitric acid and hydrochloric acid as above, filtering, fusing the residue with sodium carbonate, adding water and suphuric acid (conc.), evaporated until fumes are given off, passing through a Jones reductor and titrating with $KMnO_A$. Copper was determined in the third sample of pyrite. It was dissolved as above, noutralized with ammonia, made slightly acid with hydrochroric acid, heated to boiling and hydrogen sulphide passed in. The precipitated copper sulphide was filtered off, dissolved in nitric acid and electrolyzed. The following are the results of the analysis.

The fluxes used were limestone and quartz.

Limestone.The limestone used was a very pure white marble. It was sampled, crushed, and ground to about 30-meah 1n the sama way as the pyrite. The sample was split-shoveled to 300 grams and then bucked through a 100-mesh screen. All metallic iron present was removed with a magnet. The analysis was carried out in about the same way as in the Spathic Iron Ore Proceedure, common in the Institute Laboratories.

The analya1s was as fOllOws:

Calculated.

Quartz. The quartz was the same used in the thesis of Messrs. Bradford and Gibbons, Jr., in 1908. The1t analysis gave:

For use in the smelt the quartz was broken up by hand to pass through a 30 mm. screen. The fines were not removed. Fuel. The fuel used was Everett coke taken from the Institute bins. A sufficient quantity was put aside for the run and sampled by reserving a piece from every fourth shovelful. The sample was broken by hand, then crushed and ground in the same way as the pyrite. It was aplit-shoveled down to 100 grams and this amount bucked through a 100-mesh screen. The following

is "approximate" analysis of the coke.

The ash gave, upon analysis,

In the subjoined Table I are assembled the results of

the above analyses.

For convenience in calculating the slag the percentage of magnesia and aluminas were changed into equivalent percentages of lime and added to the CaO column. This was done as follows.

Mol. Wt. of CaO x % Al₂ $0\frac{1}{3}$ Equivalent % of CaO .
Mol. Wt. of A_{2}^{1} $0\frac{1}{3}$

Mol. Wt. of CaO x $\cancel{\%}$ MgO = Equivalent $\cancel{\%}$ of CaO.
Mol. Wt. of MgO

Table No. I is thus changed as given below in Table No. II. $\mathcal{L} = 2.55$ $\hat{\boldsymbol{\cdot}$

DESCRIPTION OF THE BLAST FURNACE.

The blast furnace of the laboratory is similar to the Arizona copper blast furnace. It consists of a water-jacketed boilar shell resting on four cast iron columns. The working height 1s 46" and the distance from the bottom to the level of the tuyerss is 14 ". The diameter at the top of the furnace is $23-1/4$ " and at the bottom $17-1/2$ ".

There are seven tuyeres $-$ - four $1-3/8$ " and three 2" in diametar. The bustle pipe is 6" in dlamster. This ie shown in the drawing.

The crucible was put in the furnace as follows: the bottom plate was placed in position and clamped. Then a mixture of 3 parts coke, 1-1/2 part ashes and 1 part fire clay, was introduced through the charging door and tamped firmly into place. The furnace was filled up to the level of the tuyeres with this material firmly tamped down. Then the plate which closed the breast of the furnace was removed and the central part of the compact brasque dug out leaving the crucible with the cross section ahown in the drawing.

THE BLOWER.

The blower which supplied the air to the furnace is a Root No. $1/2$. It has a rated capacity of 487 cubic feet of free air per minute, running at a rats of 325 R. P.M. The blast main is 6" in diameter.

The volume of air furnished to the furnace was measured with a Pitot tube and two U-tube manometers, giving respectively the static and velocity pressure heads.

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Static Pressure.

CALCULATION OF CHARGE.

It was decided to smelt a mixture of equal parts of matte and pyrite and to pruduce a matte with 30% copper and nickel.

Starting with 50 Kgs, matte and 50 Kgs, pyrite. The mixture contains 5.40 Kgs. Cu, 1.17 Kgs. Ni and .21 Kgs. Total = 6.78 Kgs. Cu, Ni, Pb. $Pb.$ These 6.78 Kgs. = 30% of Wt. of matte, Hence $\frac{6.78}{30}$ x 100 = 22.6 Kgs. is the Wt. of matte to be preduced per 100 Kgs. ore. New 5.40 Kgs. copper = 6.76 Kgs. Cu₂S 1.17 $N1 = 2.13$ " $M_{3}S_{2}$ " Pb = 0.24 "
Total = $\frac{0.24}{9.13}$ " 0.21 Pb S Matte.

The FeS in the matte will be

 $22.60 - 9.13 = 13.47$ Kgs.

To supply the FeO necessary for this 13.47 x FeO = 11.03 Kgs. $\overline{\mathrm{FeS}}$ 12 Kgs. coke per 100 kgs. matte and pyrite were used.

A fermer run, similar in character to the present one showed that an addition of 12 Kgs. coke to 100 Kgs. of ore would supplement the heat generated by the combustion of iron and sulphur -- hence the same amount of fusl this time.

The slag chosen had the following composition: Si 0_2 ' 36.8 $\%$; FeO, 51.2 $\%$; CaO, 12.0 $\%$. It lies within the range of pyritic slag.

The table No. III shows that the proposed charge

contains 62.29 Kgs. FeO.

From this total will have to be deducted the number of Kgs. FeO going into the matte.

62.29 - 11.03 = 51.26 Kgs. Fe0 to be fluxed.

The Silica necessary for this FeO equals $\frac{36.8}{51.2}$ x 51.26

 $= 36.84$ Kgs.

Table Ne. III shows that there is 6.00 Kgs. silica present. to be supplied equals $36.84 - 6.00 = 30.84$ Kgs. Hence, $S1$ 0 The quartz used contains 95.53 $\%$ available SiO2' $rac{30.84}{95.53}$ x $100 = 32.29$ Therefore quartz that has to be added

To find the CaO necessary the silica was used as the basis of calculation. As shown by table Nc. III there are now present 37.20 Kgs. of $$10₂$. CaO necessary for this is

 $\frac{12}{36.8}$ x 37.20 = 12.14 Kgs. There are already present 1.37 Kgs. CaO. Hence the CaO to be supplied is

 $12.14 - 1.37 = 10.77$ Kes. The limestone contains .35% FeO. As this is equivalent $\frac{\text{to }12}{51.2}$ x .35 % Fe0 = .08% Ca0, there is 55.73 - .08 = 55.65% CaO available in the limestons. Hence, the limestone necessary to furnish the CaO is

 $\frac{10.77}{55.85}$ x 100 = 19.36 Kgs.

TABLE NO. III.

DESCRIPTION OF RUN AND DATA SHEETS.

The furnace was blown in at 8.45 AM. The blowing in charge consisted of paper, kindling wood, charceal, coke, copper slag and some fine copper matte. The individual charges and the order in which they were fed are shown in the weigher and feeder's data sheets. The blowing in charges were the same as those used in the laboratery for blewing in the blast furnace for a normal reducing fusion. The furnace, filled with the blowing in charge. was lighted, later, a tuyere was inserted in the tap-hole and a gentle blast turned on. This was kept going until the charceal and coke were burning freely. Then the four $1-3/8$ " tuyeres were inserted and the furnace run a while until it got het encugh for the pyritic charge. Now the three 2" tuteres were put in and the regular pyritic charges of 100 Kgs. of ore and flux with 8 Kgs. of coke fed.

During the run the following reads were taken: temperature of jacket water at inlet and outlet, static and velocity heads of the blast, moisture (Grains per cubic fect) in the air, baremetric prassure, atmospheric temperature, and the temperature of the slag. The jacket water was measured at intervals by weighing the overflow during a half minute. Chilled slag samples were obtained from every slag part. Two flue gas analyses were also mede during the run.

The furnace worked very well, the slag showed great fluidity and the same wes the case with the matte of which a very large amount was produced. An artificial bosh was formed in the furnace as shown by the drawing, the tuyeres were black most of the time, but the blast penetrated the wall accretion without difficulty.

The run lasted till 2.15 P. M. The total amount of materials fed was 230 Kgs., slag; 236.8 Kgs., matte; 216.9 Kgs., pyrite; 139.9 Kgs., quartz; 72.1 Kgs., limestone; and 84.1 Kgs., coke.

WEIGHER.

			Charge Coke.		$O_{re.}$	$F/\nu x$.				
	Time. weighed				Matte Pyrite	S lag.		Quartz Limest!	Signature.	
	8.45	1			3 Aods Kindfing		3 hods Chapcoal			
		$\mathbf{2}$	36							
		\mathcal{S}	18			50				
	9.10	$\frac{1}{2}$	18°			100				
	9.20	5 ²	18	20	σ	\mathcal{F} O	σ	$\mathcal O$	H.R. Perry	
	19.45	ϵ	8°		33.433.4			21.3 12.8	\mathbf{r}	
	10.00	$\overline{}$	$\boldsymbol{\mathcal{G}}$		33.0 33.0			2 3 12.8	t, ι,	
$\sqrt[3]{}$	10.37	8 [′]	δ	35.0	3300		213128		s.	
	$\frac{1}{2}$ 47	9 [°]	8 ²	330	320		213	$ 12.\xi $		
	10.55/0		δ	-330 330			2 3	12.8		
	$[\cdot 5 $	$\vert \vert$	8		33.0 330		213	12.8	\mathbf{t}	
	11.45] 12 4.6 18.8 18.8								12.1 7.3 used a natio of .57	
	12.43/3		$\mathscr N$.						Tel of Pyritic Smelt 620 pres	
	125914					$/$ v D			A z	

 $\frac{1}{2}$

 $\tau_{\rm b}$ FEEDER Chrg Feed door Top Flue Gas
No. Top Chrg Hot-Cold Time Temp Signature. Time Coke Charge 3 hodz Kir 3 hods Charcoul \prime $\overline{2}$ 3 $\overline{4}$ $5|3$ uncher $Coleq$ 9.25 N.R. Perry The che $\left| \frac{1}{\sqrt{2}} \right|$ 6 2.6 H_2 -10.377 \mathcal{L}_k Color -10.4581 池 Warry gasanaly -10559900 malp \sim 11 $\,$ \rightarrow $1.3''$ cold 11.15^{-} 11.3710 gas analysis
made at $11 | 2'$ 0" w am 12.04 11.55 Temp (te 12°F auto $16''|z_13''$ $|223|$ $|2|$ $|12.43|$ 13 2 0 aut 01 d /d $18.$ $12137/9$ $z's'$ z' ゚゙゚゙゙゚゙゙゙゙゙゚゙

ASSISTANT TAPPER

 $\sim 10^{-1}$

X Pyritic fuelt.

TAPPER.

 \mathcal{A}

br = bright bk = black
dr = dark

 $\mathcal{L}^{\text{max}}_{\text{max}}$, $\mathcal{L}^{\text{max}}_{\text{max}}$

Time.	S/ag	Hygrom. Barom.	No. Reading Pressure.	Remarks.	Signature.
9.50 1		41.3		29.88 Thick-Quite warm	$R.L.B_{EA}/ES$
10.02 2		39.50	29.88	H ot - More fluid.	$R.$ L. BEALES
10.10	$\overline{3}$	40.50	$\tilde{\mathbf{r}}$.	\mathbf{r} and \mathbf{r}	$\bullet\bullet$
10.13 +		$\frac{1}{2}$, $\frac{1}{2}$	\mathbf{Q}^{max}	\int fluid	$\begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}$ $\hat{\mathbf{v}}$
10.20 J		α	\cdot	$\label{eq:1} \mathbf{e}^{(1)} = \mathbf{e}^{(1)} \mathbf{e}^{(1)} \mathbf{e}^{(1)} \mathbf{e}^{(1)}$	\mathcal{L}_{max} \mathcal{L}_{max}
10.26 7		454	θ	" first matte	$\mathbf{u} = \frac{1}{2}$ $\boldsymbol{\eta}$
10.3399		$\begin{matrix} 1 \\ 2 \\ 3 \\ 4 \end{matrix}$	\mathbf{q}^{\dagger}	"Veryliguid -	$\mathcal{L}(\mathcal{A})$ $\mathbf{a} = \mathbf{b}$
10.40 10		. 8	$\langle \hat{\mathbf{u}}_i \rangle$	$\alpha_{\rm{max}}=0.00000$	$\mathbf{G}^{(n)}$ $\mathcal{M}_{\mathrm{eff}}$
1055 11		SO_{15}^{\times}	29.90	$\frac{1}{4}$ and $\frac{1}{4}$	B Wohlquurth
11.00 /2		$\overline{1}$	$\mathcal{L}^{\mathcal{L}}$		
11.03	13	$\epsilon_{\rm f}$	4	Pyritic smelt	B Wohlgewith
11.14 11.24	14 15	44 4J	\cdots $\bullet\bullet$	Luquid Lot	\mathbf{u}
11.32 11.36	_/_6 _ 17	$\langle \mathbf{C} \mathbf{r} \rangle$ $\mathbf{f}(\mathbf{f}^{\mathrm{in}})$	u $\bullet\bullet$	Temp sloy noor C Temp slag 1120 C	\sim 0.
11.46 1200	18 19	t c	$\overline{}$	Large aunt motte	
1216	20	$3.6g$ r per	.,	Temp 1120°C	. .
12.22	2 _l	3.69	Ħ	1130 ''	
1232	22	v	٠,	1140 $\boldsymbol{\prime}$ 1140	$^{\prime}$
1.44 12.57	2 ₃ 24	n	$\prime\prime$	H 18.30	n
1.1 _D	25	Ħ	¥.	AT lo'clock powercutof	,.
1.25	26	t,		" 1:3mm power on.	
137	27	$^{\prime}$			\cdots
153	28	\cdot f		Blowing out	,,

SLAGMAN.

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 $\hat{\mathcal{A}}$

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CLEAN UP.

The products of the smelt were divided into pyritic slag, pyritic matte, preliminary matte, preliminary and final slag and odds and ends. Towards the end of the pre-Iiminary run, the pots were kept in the order in which they were filled, so as to keep separate the preliminary slag and matt from the pyritic and to distinguish them when cold by the difference in appearance of the slag. The preliminary end also the final slag were black in color, vitreous in lustre while the pyritic slag was black but was dull and non-vitrecus. All the matte produced after that which had been fed with the blowing in charges was considered to be pyritic matte. The odds and ends included the crnst forming the. bOsh or wall accretion, the matte-scaked portion of the crucible, and the material drawn from the furnace after the last tap excepting the unburned coke which was picked out by hand.

It was decided not to sample and analyze the preliminary matte, as, being equal in weight to the matte added during the preliminary run, its composition was assumed to hewe remained unchanged, excepting the amount of copper that it probably took up from the blowing in slag. All other products were broken by hand to about egg-size and then sampled by fractional selection. A hod of each was preserved as a sample, and a hodful crushed, ground, and bucked to pass a 100-mesh screen in the same way as was done with the samples of ore for the smelt.

The products of the run were anal-Analysis of Products. yzed for their copper, nickel, and sulphur contents. In addition, there were determined, in the pyritic matte, the iron, in the chilled sample of the pyritic slag, the Fe0, SiO₂ Ca0, Mg0, and $A1_2O_3$. The methods of analysis were similar to those used with the raw materials of the smelt. Some difficulty was experienced in determining the copper electrolytically in the pyritic slag and in the odds and ends. The results were checked by the method of ttration with potassium iodate (KIO₃) devised by C. S. Jamieson, L. H. Levy, and H. I. Wells and published in the journal of the American Chemical Society, 1908, Vol. I, Page 760.

Materials Cu Ni S \mathbf{Fe} Matte 8.73 1.95 26.25 58.65 Pyritic Slag 0.76 0.06 2.75 Prel. & Final 0.28 0.00 1.48 Slag. Odds & Ends 1.59 0.29 2.51

TABLE NO. IV. ANAINSIS OF PRODUCTS.

GAS ANALYSIS.

ACCOUNT OF STOCK.

The blowing in charges contained 20 Kgs. of matte, the analysis of which was not known. For this reason, a complete account of the copper is not possible.

. The first 20 Kgs. of matte produced resulted from the matte mixture and foul slag used in the blowing in and was assumed to contain all copper not accounted for in cther products. The balance sheet was made, using this λ assumption.

The balance sheet of sulphur was calculated only forthe pyritic run.

BALANCE SHEET OF MATERIALS.

 $#$
This analysis unknown as it was decided just before the

run to add the matte mixture.

TABLE NO. VII.

 $#$

Since the Cu in the matte used when blowing in is notknown a complete account of the Cu is not possible.

BALANCE SHEET OF SULPHUR.

TABLE NO. VIII.

TABLE NO. IX.

Materials	Weight	Sulphur.				
Produced.	Kgs.	℅	Wt. Kgs.	$%$ of total		
Matte	216.4	26.25	56.80	84.49		
Pyritic Slag	256.0	2.75	7.04	10.50		
Odds & Ends	134.4	2.51	3.37	5.01		
Total	606.8		67.21	100.00		

CALCULATION OF THEORETICAL BALANCE SHEET OF MATERIALS

FOR ONE PYRITIC CHARGE.

There are three methods of calculating a Theorstical Balance Sheet of Material. They are based on, (1) total materials; (2) definite weight of matte produced; (3) materials of a single charge.

The irregularities in ths running of the furnace during blowing in and blowing out make it difficult to ohtain reliable data for these two periods and also to define the limits of the run proper. The same holds good for making a definite amount of matte produced, the basis of calculation. In the third method, these errors are avoided, as the calculations are based upon data taken while the furnace is running normally. It was therefore chosen fer making a theoretical balence sheet of material.

 $Sinee$ the heat required to smelt the charge depends largely upon the form in the elements ara chemically combined, it is necessary to calculate a rational analysis of the materials charged. This is done as follows: Matte. From the analysis of the matteit is known that the iron is present as FeS, FeO, $Fe₃O₄$ and the remainder is assumed to exist as metallic iron. The amount of oxygen present is assumed to be the per cent not avountad for in the chemical analysis. With these assumptions, the amounts of FeS, FeO, $Fe_{3}O_{4}$ and Fe were calculated as fcllcws:

Iron present is FeS.

This is found by calculating the sulphur necessary to unite with the Cu, Mi, and Pb present to form $\mathrm{Cu}_2\mathrm{S}$, $\mathrm{N}_3\mathrm{S}_2$ and Pbs and assuming the remaining S to exist as FeS.

Total sulphur present = 25.94% S as Cu₂S Ni_3S_2 and Pbs = 3.34% S to form FeS is $25.94 - 3.34 = 22.60%$ Fe equivalent to this Sulphur as FeS $\frac{56}{32}$ x 22.60 = 39.46% FeS present equals 62.06%

The amount of FeO present is determined by assuming it is in the tratic 40 to the silica present, that is, that it is in the form of slag pellets.

Silica present equals .63%

Fe0 present equals $\frac{40}{30}$ x.63 = .84%

This is equivalent to .65% iron and .19% Oxygen. The remainder of the iron exists as Fe₃0₄and metallic Fe. The amount of oxygen in the $Fe_{3}O_{4}$ is obtained by subtracting from 100% the total percentage as found by analysis (95.11%) and the percent cxygen in the FeO(.19%). This leaves $\frac{1}{2}$.70% as the amount of oxygen combined with iron in the form of $Fe_{Z}O_{A}$.

Fe in Fe₃0₄ that is equivalent to 4.70% $0 = 12.34\%$. This gives 17.04% of $Fe_{Z}O_{A}$.

The remaining iron is the metallic iron and its per cent is found by subtracting from the total Fe, the amount present as FeS, FeO, and $Fe_{3}O_{A}$.

 -55 , 32% Total Fe equals

 $12,34$ = 2.87% Metallic Fe equals $55.32 - (39.46 .65)$ The Alg 03, Ca 0 and Si 0₂ are assumed to exist in

that form.

Pyrite. The pyrite contains 1.25% Cu which is assumed to exist as Cu₂S. The remaining S is considered to be in

the form of FeS and FeS₂, the amount of each being calculated as follows:

S as FeS and Fe $S_2 =$ total S - S as Cu₂S.

Total S equals 45.11% .

S as $C\psi$ S equals. 32%.

S as FeS and FeS₂ = $45.11 - .32 = 44.79%$. Fe as Fes and $FeS_2 = \text{total}$ Fe = 40.62%.

Now Let $X = \frac{8}{100}$ Fes, then $\frac{32}{88}$, $X = \frac{8}{100}$ S as FeS.

" $Y = \frac{64}{120}$ $Y = \frac{64}{120}$ $Y = \frac{64}{120}$ S as Fe S₂.

Also the \leq FeS + \leq FeS = \leq Fe + \leq S as $F e S$ and FeS₂.

S as FeS and FeS $_2 = 44.79 = \frac{32}{88} \times \frac{64}{120}$ Y (1) (2) $X + Y = 40.62 + 44.79 = 85.41$

From equations (1) and (2)

 \mathcal{F} res = X = 4.51% $\frac{1}{2} \text{ FeS}_2 = \text{Y} = 80.90\%$

The $A1_20_3$ and Si 0_2 are assumed to exist in that form. The remaining .83% unaccounted for by analysis is assumed to be water of crystallization in the aluminum silicate.

QuartzThe SiO₂, FeO and Alo₂, are assumed to exist in that form. The remaining 1.40% unaccounted for by the analysis is designated in the table No. XII as X. It is assumed to be slag-ferming material.

The CaO, MgO, FeO, and SiO₂ are recorded Iimestone. as obtained by analysis. The 44.15% unaccounted for is assumed to be CO₂.

The proximate analysis based on dry coke gave Coke. 77.02% fixed carbon and 16.22% ash. The sulphur in the latter probably exists as SO_3 (.61%). The SO_3 is volatile at the furnace temperature leaving 15.61% of slag-forming material. The 6.76% unaccounted for is the volatile matter in the coke. The moisture accompanying the 7.91 Kgs. of coke, as obtained by analysis, is .73 Kgs. .

Calculation of Blast.

There are two methods of calculation of the blast, one using the flue gas analysis and the amount of carbon per charge, the other by means of Pitot tube measurements of velocity head and static pressure head.

Method Using Gas Analysis.

The volume of flue gas is first calculated by dividing the total weight of carbon in one charge by the weight of carbon (as CO and CO₂) in 1-m⁻ of gas. Average Gas Analysis.

CO₂, 19.85%; CO, 2.60%; SO₂, 25%; O, 50%; N, 76.80%.

C in 1 m of flue gas = ($\%$ of CO₂ in flue gas $\%$ CO in flue gas) x (Wt. of C in 1 m^3 of CO or CO₂ under standard conditions). Wt. of C in 1 m 3 of CO or CO gunder standard conditions = $5\frac{4}{5}g$. \blacksquare \blacks $.026$) x $.54 = .12$ Kg. Carbon entering gas from coke = 6.09 Kgs. (See Table XII.) limestone = $\frac{12}{44}$ x 5.64 = 1.54Kgs. Total carbon in gas = C from coke $+$ C from limestone. \blacksquare \blacksquare 6.09 + 1.54 = 7.63 Kgs. Volume of flue gas per charge at 0° C and 760 mm. $=\frac{7.63}{12}$ = 63.58 m³ It was assumed that all the nitrogen in the flue gases was that introduced by the blast. Volume of $N = \mathbb{Z}N$ in flue gas x volume of flue gas. Volume of $N = .768 \times 63.58 = 48.83 \text{ m}^3$. Volume of air = $\frac{\text{volume of N}}{\% \text{ of N in air}}$ x 100. \mathcal of N in air = 79.2 \mathcal by volume. Volume of air to furnish 48.83 m³ N equals m^3 dry air at 0 and 760 mm. $\frac{48.83}{79.2}$ x 100 = 61.65 Wt. of 1 m^3 dry air at 0^0 and 760 mm. = 1.293 Kgs. $"61.65""$ * $= 79.71$ Conditions at time of run. Atmospheric temp. = 69° F = $20\frac{\circ}{5}$ $\mathbf C$ Barometric pressure = 29.90 = approx. standard. 61.65 m³ dry air at 0⁰ and 760 mm. = 293.5 x 61.65 = 66.28 m³ dry air at 20.95 C and 760 mm.

The moisture acccmpanying this air is calculated as . fOllows:

Hygrometer readings gave 3.6 grains water to cubic foot air.

3.6 grains par cubic foot equals 8.27 grams per $m³$. in blast per charge $=$ Vol. of blast x Kgs. $_{20}$ per m 3 Wt.HoO " " " " $=$ $\frac{66.28 \times 8.27}{1000}$ = .55 Kgs. H20.

Method using Pitot Tube measurements.

The volume of the blast was calculated from the Pitot tube measurements as fOllows:

Vol. of air percharge = (Vel. per Sec.) x (A.of cross section of pipe (x, x) (of one charge in passing through furnace in seconds).

The velocity is calculated by the formula $V = \sqrt{2}$ gh where h is the velocity head in terms of air. Velocity head $= .61$ " water.

Water is 772 x as heavy as air at 0⁰ and 760 mm.

Therafcre velocity head = .61 x 772 = 470.9" air = 39.24' air. .
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Substituting in the formula

 $V = \sqrt{64 \times 42.55} = 52.08'$ per sec.

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Area of cross section of blast main $=$.195 sq. ft.

Rate of charging equals one charge in 21 minutes or 1,260 sec. Static pressure head = $6.97"$ water = 1/4 lb. per sq. inch.

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Therefore Vol. of air par charge $= 52.08 \times .196 \times .1260$

 $=$ 12865 cu.ft. air at 2 \mathcal{C}_0 , 5 and 1/4 lb.

o
12865 cu. ft. air at 20.5 and 1/4 1b. 364 m 3 cu. ft. air at 20.5 " .. II " $=$ 364 m³ at 20.5 k1/4# $=$ 344 " air at 0 $^{\circ}$ and 760 mm.

 $NOTE$. There is a great difference between the volumes of air cbtained by the two methods. This is due either to faulty gas samples or *to* the lack of calibration of the Pitot tubas or to both. The vOlume calculated from the gas analysis was used 1n the calculations , and not that obtained from the Pitot tube measurements, as the gas analysis had to enter the calculation of the heat balance.

The materials are distributed under the heads of Matte, Slag and Gas. The copper, nickel, and lead are all figured as entering the matte, the small amounts in the slag are assumed to exist there as matte particles'. The weight of matte produced from one charge was calculated from the weight of copper in the charge and the per cent of copper in the matte produced. The weights of iron and sulphur entoring the matte were calculated frcm the analysis of the matte formed. All solid substances not entering the matte were assumed to form slag and the remaining vOlatile and combustible matter to enter the gas.

Wt. matte produced per charge $=$ $\frac{wt}{z}$. Cu per charge x 100. Wt. Cu per charge $= 3.55$ Kgs. $\%$ Cu in me.tte $\frac{1}{2}$ =8.73%.

Matte produced per charge = $\frac{3.55}{8.73}$ x 100 = 40.67 Kgs.

The sulphur is assigned as follows:

The Cu₂ S, $N1 S$, Pbs, and FeS (amounting to 27.62 Kgs), were assigned to the matte. These contained 9.20 Kgs. sulphur. The sulphur in the matte produced is 26.25% (by analysis). Therefore, the 40.67 Kgs. of matte contain 10.68 Kgs. sulphur. The amount of S still to be furnished = $10.68 - 9.20 = 1.48$ Kgs. This is equivalent to 3.67 Kgs. FeS which must be furnished by the FeS₂. The remaining sulphur is assigned to the gas. The iron is assigned as follows:

The total iron entering the mate as indicated above Bquals 16.30 Kgs.

The matte produced contains both metallic iron and magnetic oxide of iron. The amount of the latter was not determined but is estimated to correspond to 3% of oxygen. Total wt. of sulphides $= 31.29$ Kgs. The weight Fe and Fe₃ $0_4 = 40.67 - 31.29 = 9.38$ Kgs. Wt. 0 in matte = .03 x 40.67 = 1.22 Kgs. This is equivalent to 4.42 Kgs. Feg 0_4 . Wt. matallic Fe = 9.38 - 4.42 = 4.96 Kgs. The Fe₃ O₄ is assumed to be supplied by the Fe₃^O4 in the matte charged. The remainder of the latter Fe₂O_A is assumed to be reduced to FeO and O and to enter the slag and gas

respectively. The metallic iron (4.96Kgs.) is assumed to c come from the Fes_2 . Of the Fes_2 , 8.63 Kgs. (4.96 Kgs. as Fe and 3.67 Kgs. asFeS) enter the matte,. The Fe (5.30 Kgs) is assigned to the slag and remaining S (I2.74 Kgg.) to the gas.

The assignment of the remaining materials requires no comment except that of the I.76 Kgs. of 0 from the blast which is assigned to the slag. It is the 0 required to oxidize the metallic iron from the matte charged and the iron which enters theslag from the FeS2.

THEORETICAL BALANCE SHEET OF MATERIALS.

TABLE No.XII.

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 \sim $\mathcal{L}^{\text{max}}_{\text{max}}$, where $\mathcal{L}^{\text{max}}_{\text{max}}$ $\sim 10^{11}$

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 $\label{eq:2.1} \begin{split} \mathcal{L}_{\text{max}}(\mathcal{L}_{\text{max}}) = \mathcal{L}_{\text{max}}(\mathcal{L}_{\text{max}}) \,, \end{split}$

 \sim

 \mathcal{A}

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 \sim

 $\frac{1}{\sqrt{2}}$

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 $\mathcal{L}^{\mathcal{A}}$

 $\sim 10^{-1}$

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 $\sim 10^{11}$ and $\sim 10^{11}$ km s $^{-1}$

 $\sim 10^7$

THEBMAL BALANCE.

The figures used for heats of formation, specific heats, etc. are those given by J.W.Richards in his "Metallurgical Calculations". Those marked "approx". do not apply directly to the materials in this case. Eut since determinations of specific heats, heats of fusion, etc. on thedifferent materials were not practicable, figures were selected which seemed to apply most nearly to each case.

Heat Generated.

- (I) Oxidation C to $CO₂$ (8100 Cal. per Kgs. of C)
	- C burned to $CO_2 =$ (Vol. of gas X $\%$ CO₂ X Wt. C in 1 \texttt{m}^3 CO₂) = (Wt. C in CO₂ from lmste

 $63.58 \times .1985 \times .54 = 6.83$ Kgs.

 $6.83 - 1.54 = 5.29$ Kgs.

 $5.29 \times 8100 = 44,793$ Cal.

(2) Oxidation C to CO. (2430 Cal. per Kg. C.)

C burned to $CO = Total C in code - C burned to CO_2 .$ $6.09 - 5.29 = .80$ Kg.

 $.80 \times 2430 = 1944$ Cal.

(3) Oxidation S to SO₂ (2164 Cal. per Kg. S)

% SO₂ in gas x m³ of gas = m³ of SO₂. (Gas analysis) of $SO_2 \times S_1 = Wt$. Sin 1 m³ SO_2 Wt. of 1 m H x Density

of SO_2 .

3 .0025 \times 63.58 =.159 m of SO

2 .159 (.0896 x 32 x $\frac{32}{10}$ = .227 Kgs. S burned. This does not agree with the of S assigned to gas in the theoretical balance sheet. The difference is assumed

- to have been distilled off as free sulphur. $.227'x$. 2164 = 491 Cal.
	- (4) Oxidation of Fe to FeO. (1173 Cal. per Kg. Fe.) Wt. Fe oxidized = .95 $5.30 = 6.25$ Kgs. (See Table *No.* XII)

6.25 x 1173 = 7331 Cal.

- (5) Heat *ot* Formation of Matte. All copper and iron exist as sulphides in the ore. The heat of union of FeS andCu₂S is unknown.
- (6) Heat of Formation of Slag. (150 Cal. per Kg. approx.) Wt. slag made = 43.59 Kgs.

 $43.59 \times 150 = 6538$ Cal.

o (7) Sensible Heat in Blast at roam temp. (20.5) (Sp. Heat .25 approx.)

Vol. x Sp. Ht. x Temp. = 66.28 x .3036 x 20.5. = 413 Cal.

o (8) Sens1bleHeat in Charge at room temp. (20.5)

(Sp. Heat = .25 approx.)

Wt. xSp. Ht. x Temp. = 107.91 x .25 x 20.5 = 553 Cal.

HEAT ABSORBED.

- (a) Reduction of $Fe₃O₄$ to FeO. (1023 Cal. per Kg. FeO.) Wt. FeO from Fe_3O_4 = 1.11Kgs. 1.11 x1023 =ll35'Cal.
	- (b) Reduction Fes_2 to Fe (428 Cal. per Kg. Fe Approx.) The heat of reduction of FeS_{2 to} Fe is not known., Since it probably is not much larger than FeS to Fe,

the latter figure is used.

Wt. Fe from $Fes_2 = 10.26$ Kgs. (See distribution of matte constituents, page 34.)

 $10.26 \times 428 = 4391$ Cal.

- #
- (c) Decomposition of Limestone. (1026 Cal. per Kg. C02) $#$ Figure for CaCO₃ to CO₂ used since the amount of $MgCO₃$ is small.

Wt. CO₂ from CaCO₃ = 5.64 Kgs.

 $5.64 \times 1026 = 5787$ Cal. $\frac{1}{2}$ 0

- (d) Heat in Slag (Temp. = 1130 $C.$) Heat in melted slag at 1100[°] = 300 Cal. per Kg. (approx. $43.59 \times 300 = 13077$ Cal.
	- o 0 To heat from 1100 to 1130 C. (Sp. Ht. = .27 approx. $43.59 \times .27 \times 30 = 353$ Cal.

Total Heat = $13077 + 553 = 13430$ Call.

o (el Heat in Matte. (Temp. = *1130* C) \bullet \ddots Heat in melted matte at $1000 = 200$ Cal. (approx.) $40.67 \times 200 = 8134$ Cal. o 0 To heat from 1000 to 1130 (Sp. Ht. = .285 approx. $40.67 \times .285 \times 130 = 1507$ Cal.

Total Heat = $8134 + 1507 = 9641$ Cal. \mathbf{I} 0 \mathbf{I} 0 \mathbf{I} 0 \mathbf{I} 0 \mathbf{I} 0 \mathbf{I} (f) Heat in Gases. (212 $F = 100$ C.)

(1) CO + N + O = 79.90% .

(These gases have same specific heat.)

.7990 \times 63.58 = 50.80 m^3

Sp. Ht. per $m^3 = (.303 + .000027t)$

 $Heat = 50.80 \times 100$ (.303 + .000027 x 100) =

1553 CAL.

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\n(2) Vol. of
$$
002 = .1985 \times 63.58 = 12.62 \text{ m}^3
$$
.
\nSp. Ht. per m³ = (.37 + .00022t).
\nHeat = 12.62 x 100 (.37 + .00022 x 100) =.
\n495 Gal.
\n(3) Vol. of $SO_2 = .0025 \times 63.58 = .16 \text{ m}^3$.
\nSp. Ht. per m³ = (.36 + .0003t).
\nHeat = .16 x 100 (.36 + .0003 x 100) = 6 Cal.
\n(4) Wt. evaporated = .73 + .27 + .55 = 1.55 Kgs.
\nHeat of Vaporization at 0 $= 606.5$ Cal. per Kg.
\n1.55 x 606.5 = 940 Cal.
\nSp. Ht. of Gas per Kg. = (.42 + .000188t).
\nHeat = 1.55 x 100 (.42 + .000188 x 100) =
\n68 Cal.
\nTotal Heat in gases = 1553 + 495 + 6 + 940
\n+ 68 = 3162 Cal.
\n(g) Heat in cooling water.
\nTemp. of Overflow = 92.1 C.
\nRate of Flow = 14 Kgs. per minute.
\n* " " = 147 Kgs. per charge.
\n147 x (92.1 - 12.1) = 11.613 Cal.

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XIII. THERMAL BALANCE FOR ONE CHARGE.

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SUMMARY.

The sulphur elimination obtained in this run was 56.38 par cent of the sulphur present, instead of 79.64% as expected. If the analysis of the flue gas is correct about 98% of the sulphur eliminated was driven off in the form of sulphur vapor and not as sulphur dioxide. The sample of gas must have been faulty, as the concentration obtained, --1.6 into $1 -$ gives a greater pyritic effect although it falls below the calculated concentration of 4.4 into 1.

The thermal balance shows thatthe larger part of the heat. in the furnace was furnished by the coke and not by the oxidation'of the iron and sulphur as should have been the case.

The slag formed contained 32.37 $\%$ FeO instead of the calculated 51.2%, the silica contents was 41.98% instead of the calculated 36,08%. The percentage of lime ran much higher than was intended. These facts show that sufficient silica was present but thatthe iron was not oxidized and therefore could not enter the slag but went into the matte. Assuming the air supply to be sufficient, the coke must have prevented the desired pytitic effect. الكاورا

A decrease in the amount of coke used would there-.. fore correct the smelting conditions.