The Sintering of Fine Ferro-Manganese Ore with the Elimination of Lead and Zinc.

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Purpose of the Investigation.

The ferro-manganese ore produced from the Taiyo Mine in Kemaman, Trengganu Kingdom, Malay, is, on the whole, fine, and therefore not only is there much loss by dusting when charging the iron blast furnace or open-hearth steel furnace with the raw materials for the manufacture of iron or steel, but the ore is troublesome to convey and handle as, in open storage, it is rendered plastic by rain. Further, as it contains a certain amount of lead and zinc in addition to iron and manganese, the lead is reduced to metallic lead in the blast furnace and settles to the bottom where it is likely to cause a breakdown of the bricks lining of the The zinc also is easily reduced to the bottom. metallic state. It then distils and ascends with the furnace gases to the upper part of the furnace. Here it often enters into the joints of the firebricks, becomes oxidized again, increases in volume, and causes the pushing out and breaking down of the bricks in the upper part of the furnace. It is therefore necessary that the materials of the blastfurnace charge should contain the smallest possible amount of lead and zinc. In Europe and America materials that contain above 0.8% of zinc are not generally used, and users specify that the amount of lead shall be particularly low. But the ferromanganese ore from the Taiyo Mine in Kemaman contains 3.32 to 2.52% of lead and 1.98 to 1.39% of zinc¹⁾.

Now, we carried out an investigation into the sintering of that ore and the elimination of its lead and zinc during 1934 at the Central Laboratory of the Engineering Department of Kyoto Imperial University. We describe below, in full detail, the methods employed and the results obtained.

The Ore Sample and its Chemical Analysis.

The samples used in this investigation were of two kinds. They were No. I and No. 2. Sample No. I was brought some years ago by Mr. Miyako, one of the engineers of the above mine. Sample No. 2 was sent from the Taiyo Mine specially for the purpose of the experiment. Both appeared to be fine limonite, blackish-brown in colour, the sizing and chemical analysis of which are shown in Tables I and II.

1)	" Mining	Industry	in	the	South-Sea	Islands,"	Sokichi
p. 692.							

Inch o (T	or Mesh yler)	Screen Openning mm.	Sample No. 1 Weight %	Sample No. 2 Weight %
	+1"	+ 26.67	9.62	
-1″	+ 10	-26.67	50.32	— ,
10	+20	- 1.651	15.22	
-20	+28	-0.833	6.00	
-28	+35	0.589		25.0
- 35	+48	-0.417	3 7.45	18.7
-48	+65	-0.295	4.45	16.5
-65	+100	-0.208	2.77	12.4
- 100	+150	-0.147)	8.3
- 1 50	+200	-0.104	4.17	6.7
-200		-0.074)	12.4
			100.00	100,00

Table I. Screen Analysis.

Sample No. I was a row ore as mined.

Sample No. 2 was a crushed ore all pass through 28 mesh.

Table II. Chemical Analysis.

	Fe %	Mn %	РЪ %	Zn %	Sn %	Insolu- ble %	H₂O %	Ignition loss %
Sample No. 1	30.92	18.25	3.32	1.40	0.24	6.90	1.4	12.0
" 2	29.10	21.61	2.52	1.98	0.15	5.47	243	9.68

Photomicrograph No. 1.

Sample No. 2. Magnification about 85×.



The state in which the iron, manganese, lead, and zinc exist in the ore is not fully known, but according to the chemical analysis, its appearance, and the report by Dr. Kow referred to above, we

th-Sea Islands," Sokichi Kow, Journal of the Mining Institute of Kyushu, Oct., 1930,

think that the iron occurs as limonite, the manganese as oxide, and the lead and zinc as oxide or carbonate.

We examined the structure of the sample of ore under the microscope, but could not distinctly recognize a crystalline structure as in photogroph No. I because of the porous and brittle nature of the ore.

A Consideration of the Theory of Sintering.

As, up to the present, the sintering of simple manganese or ferro-manganese ores has scarcely been published, we give in what follows a summary of the study of the theory² of sintering fine iron ore formerly published by the author.

(1) The melting temperature of iron ore varies with as the amount of the silica-content.

(2) Iron ore which contains much silica melts at 1150° C in a reducing atmosphere with carbon-aceous fuel.

(3) In the method of reducing sintering, the silica in iron ore combines with ferrous oxide to from a eutectic of ferrous ortho-silicate and ferrous oxide. The eutectic temperature is 1150°C. This becomes the binder of the ore and makes a good sintered ore.

(4) In the sintering of fine iron ore, reducing sintering in the presence of moisture is much more advantageous than oxidizing sintering.

(5) Coke or anthracite is the best earbonaceous fuel to add for the reducing sintering of fine iron ore. The amount added is 3-5%, maximum. The addition of too much prolongs the time of sintering and causes over-reduction, which is absurd for sintering purposes only.

The above applies to the case of simple iron ores. Of course, in the case of ferromanganese ores the melting temperature and the sintering temperature must be a little different from those of simple ore. We were guided in our sintering experiments by the results of the abovementioned studies.

Theoretical Consideration of the Elimination of Lead and Zinc.

Some years ago Mr. Namekata and Mr. Miyako, engineers at the mine, studied the subject of separating iron from manganese in ferromanganese ore, and eliminating lead and zinc, by means of magnetic separation and also by gravity separation. The work was carried out at the Department Mining of the College of Engineering of Tokyo Imperial University and the Ore Dressing Leboratory of the Department of Mining and Metallurgy of the College of Engineering of Kyoto Imperial University. The separation and the elimination were impossible, according to the results of their experiments. Therefore there is only one method left-that of volatilizing or distilling lead and zinc in suitable form at high temperature. The melting and boiling temperatures of metallic lead, zinc, tin, and their oxides, are as follow:

 Table III.

 Melting Temperature and Boiling Temperature of Metallic Lead, Zin, Tin and their Oxides and Sulphides.

	Meta	ls		(Oxides		Sulphides			
nula	°.	ç,	nula	°.	Volatilise		nula	°.	Vol	latilise
Chemical foru	Melting Temp	Boiling Temp	Chemical forr	Melting Temp	Beginning Temp. °C	Boiling Temp. °C	Chemical for	Melting Temp	Beginning Temp. °C	Boiling Temp. °C
Pb	327	1,555	РЬО	883	800	1,472	PbS	1,112	?	~950
Zn	419	908	ZnO	—	1,300	>2,000	ZnS		?	~1,180
Sn	232	2,270	SnO2	-	~1,500	2	SnS	870	3	~830

? unknown, > over, \sim approximately.

The vapour pressures of metallic lead, zinc, tin, and their oxides are shown by the Pressure (mm. Hg)-Temperature (°C) Curve in Fig. 1.



→ Temperature C^o

^{2) &}quot;Suiyokai-shi," Transactions of the Mining and Metallurgical Alumni Association, Vol. IV (1925) 1409-1424, Vol. V (1926) 134-144.

Journal of Iron and Steel Institute of Japan, May, 1925, pp. 431-452. Transactions World Engineering Congress, Tokyo, 1929, No. 436. Memoir College of Engineering, Kyoto, Vol. , 1931, 251-274.

³⁾ Metall u. Erz, 3 (1929), s. 62-66.

⁴⁾ Metall u. Erz, Juniheft (1929), s. 269-284.

The boiling point of metallic lead is 1555°C, according to Mr. Kohlmeyer⁵⁾. But the initial temperature of volatilization of the oxide, PbO, is 870°C according to Mr. Mott⁶⁾, above 700°C according to Mr. Doeltz7 and Mr. Graumann8, or 750°C according to Mr. Feiser. The boiling temperature of PbO was measured as 1495°C by Mr. Graumann, 1470°C by Mr. Kohlmeyer, and 1472°C by Mr. Feiser. Therefore we can take it that lead oxide begins to volatilize at about 800°C, melts at 883°C, and boils at 1472°C. Volatilization of PbO in the presence of Fe₂O₃ and SiO₂ becomes difficult making a ferrite and silicate and its vapour pressure becomes very low, but the presence of Al₂O₃, CaO, MgO, and ZnO does not exert much influence.

The relation between the volatility of PbO and the temperature varies according to the porosity of that material and the amount of its surface area. Or, the volatility of PbO increases in proportion to the rise in temperature and at the same time to the increase in porosity and surface area. It is most advantageous that lead in ferro-manganese ore should be volatilized in the state of PbO, if possible. If it is volatilized in the state of metallic lead the temperature must be about 80°C higher than otherwise required.

Metallic zinc begins to volatilize at 550° C, and the relation between the temperature and the vapour pressure is as follows, according to Mr. Feiser :—

Temperature (°C)	650	730	860
Vapour pressure (mm.	Hg) 27.5	92.5	485.0

According to Mr. Kohlmeyer the boiling temperature measured 908°C.

On the contrary, zinc oxide has very low volatility. It begins to volatilize at 1300° C and volatilizes actively at $1800^{\circ}-1850^{\circ}$ C according to Mr. Feiser. Perhaps the boiling temperature seems to be above 2000°C. Furthermore, ZnO often forms zinc-ferrite in the presence of Fe₂O₃ in roasting and sintering, and that makes the volatility very row. It is best, therefore, that zinc in ferromanganese ore should be reduced to the metallic state for volatilizing. Care must be taken that ZnO or zinc-ferrite are not formed through roasting or sintering in a strong oxidizing current of air.

In accordance with the above, therefore, it is best, from theoretical considerations, in the sintering of ferro-manganese ore with the elimination of lead and zinc, the ore to be mixed with a moderate amount of carbonaceous fuel such as

- 6) " " 6 (1909), s. 453–454.
- 7) ", ", Juni (1929), s. 267-284. 8) ", ", 3 (1929), s. 62-66.

anthracite or coke and to be heated to a temperature at least above 1000°C to 1200°C in a reducing atmosphere, so long as the ore does not melt. The lead and zinc are then eliminated by volatilization and, at the same time, the ore is moderately sintered.

The Sintering Experiments.

Samples for experiments and their charge :---The ferro-manganese ore used for this experiment was sample No. 1. This was crushed to -28mesh in a crushing roll, and one portion was mixed with 5% of Hongei anthracite ground to -65 mesh, and 4% of water was added. To another portion only 3% of water was added, without anthracite. About 2.5 gm of the sample was weight and was compressed by a hand-press into a cylindrical shape which was 10.5 mm. both in diameter and height. The compressive force could not be measured, but a fixed weight of sample was used to be shaped under nearly identical The closest attention was paid to the pressure. number of revolutions of the handle of the handpress and to keeping the briquettes of a given uniform height. In this way two kind of briquettes, one containing anthracite and another without anthracite, were formed. The technical analysis of Hongei anthracite is:

Moisture	Ash	Volatiles	Fixed Carbon
%	%	%	%
1.77	3.22	10.63	84.38

Experimental Arrangement:— The electric furnace used in the experiments and its arrangement are shown in Fig. 2. A., Body of the furnace; B., Elema electric resistance rod made by Tokai Electrode Co. like a silit made by Siemens Co. in Germany; C., Porcelain combustion tube; D., Glass cap through which the sate of sintering

Fig. 2. Furnace and its Arrangement during Sintering Experiment.





during the heating could be observed; E., Magnesia boat charged with four briquettes of the sample; F., Thermocouple used to measure the temperature. The electric furnace had four Elema electric resistance rods, and all these rods were The temperature in the connected in parallel. furnace was suitably adjusted by varying the alternating current, which was dropped from 220 volts to 100-140 volts by an autotransformer. The state of distribution of the temperature in the furnace is shown in Fig. 3. From the diagram of distribution of temperature it will be seen that only a length of about 3 cm. in the centre of the furnace was heated to a comparatively uniform temperature. There was a difference of 10°C along 5 cm. length of the boat. When it is necessary to heat at high temperatures like 1000°-1250°C or over, as in this experiment, a furnace wound with nichrome wires cannot be used continuously. This, therefore, was the disadvantage in using a furnace in which Elema electric resistance rods were employed.

Experimental Operation.—The magnesia boat was first covered by a thick bed of magnesia powder and four sample briquettes were arranged on that bed. The boat was then accurately placed in the centre of the electric furnace, which is shown as II in Fig. 3, after being preheated at the mouth of the combustion tube which was inserted in the furnace. The glass cap was fixed in the tube and heating was continued at constant temperature for about 90 minutes. The autotransformer and the rheostat were regulated by watching the ammeter to see that it indicated constantly the required heating temperature as measured by the thermocouple. The reducing roast and, at the same time, the sintering experiment, were done by heating at definite temperatures, which were 1000°C, 1050°C, 1100°C, 1150°C, 1200°C or 1250°C. After being heated for 90 minutes at each of the above temperatures, the boat was withdrawn and cooled to room temperature in the desiccator.

Measurement of Porosity.—The sintered briquette was arranged to be hung by a very fine silk cord and weight in a balance. Let the weight be W_I . Next, all the pores were filled with water by dipping the briquette in hot water at about 90°C. It was then taken out and cooled nearly to room temperature by being dipped in cold water, and weighed in water and air to give W_2 and W_3 respectively. Thus the porosity can be shown from the following equation :—

- $W_3 W_1$ = the weight of water which entered into the pores of the briquette.
- $(W_1 W_2) + (W_3 W_1) = W_3 W_2$ = the weight of water equivalent to the external volume of the briquette.

That is Porosity
$$\% = \frac{W_3 - W_1}{W_3 - W_2} \times 100.$$

The porosity of each briquette was calculated from the above equation.

Measurement of the Cross-Sectional Area and the Compressive Strength.—The sintered briquette cracked and deformed owing to the rapid evaporation of water and release of gas produced by the combustion of the anthracite. Therefore it was difficult to measure accurately the cross-sectional area, but three measurements of diameter were made by micrometer—one at the upper part of each briquette, another at the middle, and a third at the lower part, and from these the average diameter was calculated. Hence the mean crosssectional area of each of the four briquettes sintered at a definite temperature was obtained.

In measuring the compressive strength, as the top and bottom faces of the cylindrical briquettes were concaved, these faces were polished on emery paper to give planes parallel with each other. The briquette was then gradually compressed by increasing by degrees a definite pressure in constant time by means of Amsler's testing machine for tensile strength, previously arranged to record compressive strength, and the pressure at which the briquette eventually fractured was noted.

Results of Roasting and Sintering Experiments.—The two kinds of briquette, one combined with anthracite and one not, were roasted at each temperature of 1000° C, 1056° C, 1100° C, 1150° and 1200° C. The appearances of these briquettes are shown in Fig. 4. The briquette which was especially combined with 5% of anthracite was completely melted in a short time after being heated at 1250° C it was immediately taken out of the furnace, but the boat was broken.

The losses in weight of the briquettes are



shown in Fig. 5. From this it will be seen that 2.5 gm. of the original briquette, which was weighed in the rough balance, reduced to about 2.17 gm. in the briquette combined without anthracite and 1.8-1.7 gm. in that with anthracite. This loss in weight is due to the reduction at red heat of ferro-manganese ore, the evaporation of water, and the combustion of anthracite. Of course, it comes to this, that the sample which was mixed with anthracite lost the greater weight.

The reduction ratio of the cross-sectional area of the briquettes is shown in Fig. 6. The original briquette was 10.5 cm. in diameter and 86.5 mm²



in cross section, but the area decreased as the roasting temperature increased, and became noticeably reduced in the case of the briquette which was mixed with anthracite.

The change in the porosity of the briquettes during roasting are shown in Fig. 7.

The porosity falls remarkably with increasing roasting temperature, and is almost nil as the melting temperature, about 1250° C, is approached. The briquette with 5% of anthracite, in particular, shows 78% porosity when the roasting temperature is 1000°C. This shows that the briquette expands considerably at low temperature. The briquette which was mixed with anthracite markedly expands at first at temperatures below 1000°C, but the porosity falls rapidly at temperatures rising above this and is lost as the melting temperature is approached.



The compressive strength of the roasted briquettes is shown in Fig. 8.

The compressive strength quickly increases as the roasting temperature rises, and, in the case of the briquette without anthracite, it is remarkably higher than in the case of the one with anthracite. The former, which was roasted at 1220°C could not be broken by the Amsler testing machine, which had a dial reading up to 300 kg..

The briquette with 5% of anthracite expands remarkably below the roasting temperature of 1100°C, as shown in Fig. 7, and its compressive strength is almost zero. The compressive strength after roasting at 1150°C are very low. These are 16 and 30 kg/cm² respectively. As the briquette melted when roasted at 1250°C, the compressive strength could not be measured. Of course, it can easily be supposed that it would have a compressive strength over 300 kg.

Change of Chemical Composition by Roasting. –Briquettes of each kind, respectively with 5% of anthracite and without anthracite, were roasted for an hour and a half at each definite temperature from 1000°C to 1250°C. The chemical analysis of each was made and the changes in the chemical

No. of Tests	Roasting temp. (°C)	Roasting time (hr.)	Insol. (%)	Fe (%)	Рь (%)	Zn (%)
Raw ore			6.90	30.92	3.32	1.40
A ₁	1,000	1.5	12.34	31.96	1.25	1.25
A_2	1,050	,,	I 2.24	32.83	0.62	1.11
A_3	1,100	,,	12.18	33.26	0.45	0.74
A_4	1,150	,,	12.15	34-39	0.31	0.63
A ₅	I,200	,,	12.05	37.05	0.28	0.54
A ₆	1,250	,,	11.43	38.78	0.15	0.41
B	1,000	,,	10.20	37.52	1.32	0.87
B_2	1,050	,,	9.67	40.81	0.68	0.52
B ₃	1,100	,,	9.65	40.92	0.53	0.31
B_4	1,150	,,	9.65	41 31	0.45	0.26
B_5	1,200	,,	9.35	43.16	0.22	0.20
\mathbf{B}_6	1,250	Melted	in short			

Fig. 9.

Table IV. Chemical Analysis of Roasted Briquettes.

A₁, A₂... Without anthracite.

B₁, B₂.....With 5% anthracite.



composition were investigated with a view to ascertaining the degree of volatility of the lead and zinc. The results are shown in Table IV.

According to this table, lead and zinc contained in ferro-manganese ore volatilize as much as the roasting temperature rises.

The eliminating rates when volatilizing lead with or without anthracite, that is to say, in oxidizing roasting or reducing roasting, are practically equal, and lead is eliminated to the extent of 0.22-015% of lead at the highest roasting temperature, 1200°-1250°C.

The loss in volatilizing zinc is very high with anthracite or in reducing roasting, and the zinc content is 0.20% at 1209°C. On the contrary, the eliminating rate is low in the oxidizing roasting, and the zinc content only falls to 0.41% when roasting for an hour and a half at 1250°C.

In short, we concluded that it was possible to lower the lead-content to 0.15% and the zinccontent to 0.20% in the case of the best efficiency in roasting for an hour and a half at a temperature of 1200°-1250°C.

As the object of the above experiment was mainly to ascertain the state of sintering, it was carried out in a small way with a briquette weighing only 2.5 gm. Next, volatilization experiments on lead and zinc were made by using 20-25 gm. of sample.

Volatilization Experiments on Lead and Zinc.

The sample for experiment :

(1) In the volatilization experiments in which the horizontal electric furnace was used sample No. 1 of the ferro-manganese ore for test was crushed to -28 mesh in the crushing rolls.

(2) In the subsequent volatilization experiments the vertical electric furnace was employed, and ore sample No. 2, crushed to -28 mesh, was used.

The anthracite of Hongei (see the preceding technical analysis), crushed to -65 mesh, was used as the carbonaceous fuel to be combined. The calcium carbonate, barium carbonate, calcium sulphate, and magnesium sulphate, which were used according to necessity, were the pharmaceutical chemicals as provided by Japanese law.

Arrangement and Conduct of the Experiment.-(1) The sketch of the first experimental arrangement for the volatilization of lead and zinc is shown in Fig. 10. A., Erema electric resistance-type furnace used in the sintering. В.. Erema electric resistance rod. C., Porcelain combustion tube with one of the ends closed. E., Narrow porcelain tube through which air was drawn in. D., Perforated porcelain plate by mean's



of which the sample was kept to the correct length, that is 3 cm. long. F., Thermocouple.

In this volatilization experiment about 20 gm. of the sample, mixed with 8% of anthracite, was first charged into the open end of the combustion tube (the other end being closed), which was then inserted into the horizontal electric furnace as shown in the diagram. The sample was kept in position by the perforated porcelain plate shown as D to prevent the material getting out of place when the porcelain combustion tube was slowly rotated. In this experiment the tube was slowly rotated 180° every five minutes during roasting so that the ore-sample was well mixed and every part of it was uniformly roasted. A consrant volume of dry air was fed through the narrow porcelain tube E to promote the volatilization of lead and zinc, as per the arrangement shown in Fig. 10. M., Motor; R., Rotary air pump; S., Air reservoir; T., Drying tower containing calcium chloride and U-tube respectively; P., Pitot tube to measure the volume of air. Thus the constant volume of air, which was dried by calcium chloride. could be fed at will into the combustion tube. As it was difficult to arrange for continuous rotation of the combustion tube in this horizontal furnace, so that the sample could be continuously well mixed and the volatilization of lead and zinc proceed as in a rotary kiln, the tube was rotated through 180° every five minutes as stated above. But we could ascertain during the experiment that combustion tube was already a little sintered at 1000-1100°C, and the sample could not be sufficiently mixed to prevent its adhering to the inner wall of the combustion tube during rotation. Moreover, in the horizontal combustion tube a cavity was made in the upper portion of the sample as shown at H in Fig. 10. It was difficult for the dry air or the roasting gas to pass uniformly

through the sample as they escaped through this part. A second experiment was therefore made in which the sample was charged into a vertical combustion tube for the elimination of lead and zinc.

In the second volatilization experiment a vertical electric furnace was used, and the combnstion tube, with one of its ends closed, was placed in the centre of the furnace. About 25 gm. of the sample was put on to the perforated plate D, the change being ore sample No. 2 mixed with I, 3, 5, and 8.7% of anthracite, thus making four kinds. The experiment was designed so that the dry air should pass uniformly through the narrow porcelain tube E and the sample below the perforated porcelain plate D (see Fig. 11) as in the first experiment.

Results of the Volatilization Experiments.— As the roasted sample became sintered on the inner wall of the combustion tube it was not entirely mixed in the first experiment described above. The second experiment was therefore undertaken. Only four tests were made because the ventilation seemed to be unequal.

With 8% of anthracite added, the roasting was carried out at 1000° C and 1100° C for four hours. We could eliminate by volatilization to the tenor of 0.27% of Pb and 0.35% of Zn, the extent of elimination of Pb being 90.7% and that of Zn being 80.7% as the best result, that is, when roasting at 1100°C. In test No. 3, in which the volume of air was reduced to 22.2 cm³/min.,



No. of	No. of Roasting temp.	Weight of sample	Weight after	t Roasting	Anthra- cite	ite Air	Assays (%)					Elimination (%)	
Tests	(°C)	charged (gr)	Roasting (gr)	(hr)	mixed (%)	(cc/min.)	Insol.	РЬ	Zn	Fe	Mn	Pb	Zn
Raw ore	·	·· ·	'	<u> </u>		—	6.90	3.32	1.40	30.92	18.25	o	0
I	1,000	—	-	4	8	66.7	13.32	. 1.15	1.18	31.39	20,84	65.3	15.7
2	1,000	18.45	12.05	4	8	69.0	9.79	1.54	1.15	31.14	21.22	53.6	17.9
3	1,100			4	8	22.2	13.31	0.81	0.94	32.02	20.52	75.5	42.0
4	1,100	20.20	12.22	4	8	58.8	10.61	0.27	0.35	.34.33	22.65	90.7	· 80.7

Table V.Results of the 1st. Volatilization Experiment.

other conditions being the same, the lead and zinc were eliminated only down to 0.81% Pb and 0.94% Zn, the extent of elimination of Pb being 75.5% and that of Zn being 42%. The result is very low. The result of roasting at 1000°C is still worse.

In the second experiment the ore-sample was mixed with I-I5% of anthracite and the roasting temperatures were of three grade, $I000^\circ$, $I100^\circ$, and $I200^\circ$ C. Roasting was continued as above for four hours and two hours in the vertical electric furnace as shown in Fig. 11. The results are

 Table VI.

 Results of the 2nd. Volatilization Experiments.

No. of	Roasting	Roasting	Anthra- cite		Air	Sample	Weight after	Sintering		Assays	5 (%)		Elim	ination	(%)
tests	(°C)	(hr)	mixed (%)	(cc	assed :/min.)	(gr)	Roasting (gr)	grade	Insol.	Pb	Zn	SO4	Pb	Zn	SO4
Raw ore		_						-	5.47	2.52	1.98	-	0	0	
5	1,000	4	1.0	64.	5	25.0	21.30	non	10.45	1.04	0.95	-	63.9	57.5	
6	,,	"	3.0	,,		· ,,	21.00	very weak	11.07	0.42	0.67	-	85.4	70.6	_
7	,,	,,	5.0	,,		37	20.85	weak	11.26	0.34	0.41		89.1	82.2	
8	,,	,,	8.7	,,		27.6	22.75	,,	14.56	0.08	0.26		97.3	88.9	-
9	,,	,,	15.0	,,		20.0		very good	15.71	tr.	0.15	— [·]	100.0	92.4	
IO	1,100	,,	1.0	,,		25.0	21.20	very weak	11.75	0.64	1.08	-	87.5	52.3	
II -	. ,,	,,	3.0	,,		,,	21.00	"	11.86	0.28	0.82	-	90.3	64.2	
12	,,	,,	4.0	,,		,,	20.60	,,	12.20	0.24	0.46		91.8	78.2	
13	.,	,,	5.0	,,		.,,	20.55	weak	16.56	0.16	0.37		94.6	84.2	
14	,,	,,	8.7	,,		27.6	19.95	"	11.72	0.18	0.91	—	94.5	65.5	
15	000, I	2	3.0	,,		25.0	21.10	very weak	10.74	0.34	1.37	_	88.2	39. I	
16	,,	"	5.0	,,		,,	20.95	weak	11.35	0.28	0.92		90.3	59.8	_
17	1,100	,,	3.0	,,		"	20.60	,,	12.05	0.18	0.79	_	93.8	66.2	- [*]
18	,,	,,	5.0	,,		,,	20.50	good	12.58	0.08	0.41		98.7	82.5	_
19	1,200	,,	3.0	,		,,	20.00	very good	12.23	0.12	1,12	-	96.I	53.3	
20	,, .	. ,,	5.0	, ,,		,,	20.35	best	20.34	0.42	0.49		85.9	79.3	
21	1,100	4	10	,,)	"	21.75	weak	10.64	0.92	1.06		66.9	53.5	
22	,,	,,	3.0	· ,,	٥ <u>`</u>	· ,,	20.35	good	10.70	0.74	0.65		75.2	72.4	
23	2. ja 22. ja	,,	50	· ',,	S 2	,,	20.50	,,	10.63	0.56	0.42		81.2	82.1	·
24	, ,,	,,	8.o	") -	,,	,,	best	10.54	0.36	0.10		87.8	95.3	
25	1,000	2	3.0	',, \	`	· .,,	22.00	non	10.45	0.22	0.79	-	92.0	63.8	-
26	,,	,,	5.0	"		,,	21.90	"	10.84	0.20	0.51	·	92.7	76.7	
27	1,100	, ,,	3.0	. ,,	်ိဳ	,,	22.15	weak	11.19	0.22	0.34		91.9	84.3	_
28	,,	"	5.0	,,,	23 Back	"	21.35	good	11.21	0.10	0,20		96.5	91.1	
29 ^{- 1}	1,200	· ,,	3.0	- ,,		"	21.28	,, .	12.74	0.12	0.24		95.7	89.2	_
30	,,	,,	5.O	,, ,)	,,	20.00	»» .	12.29	0.22	0.09	_	92.7	96.2	
31	1,000	,,	3.0	· ,, ·) . <u>°</u> %	,,	21.40	non	11.04	1.03	1.24	3.34	63.5	44.8	23.3
32	1,100	,,	,,	. ,,	0)2()	,,	21.50	weak	12.14	0.70	1.29	1.33	75.1	42.3	69.2
33	I,200	,,	,,	' ,,	5 FUC	·,,	21.00	good	12.23	0.67	0.75	0.78	76.7	67.2	83.2
34	1,000	,,	,,	,,):_0_%	,,	21.50	non	10.81	0.71	0.69	0.70	74.8	71.3	79.1
35	1,100	,,	,,	,,	E) (S) (S)	,,	21.00	weak	13.72	0.53	1.28	o.58	81.5	43.3	83.0
36	1,200	,,	** .	. ** .) M H. (197	,,	20.00	best	14.50	0.42	1.21	0.79	86.1	49.5	78.1

given in Table VI.

A comparison of the relation between the quantities of anthracite added and the rate of elimination of the lead and zinc under the same conditions of roasting, the time being four hours, is shown in Fig. 12. There was an exceptional case in test No. 14 (which may perhaps be due to a mistaken in analysis or in sampling), but, in general, the rate of elimination of lead and zinc increases in proportion to the quantity of anthracite





added. Though the difference between roasting at 1000° C and 1100° C does not affect very much the rate of elimination of lead and zinc, the rate of elimination of lead generally shows a tendency to increase a little with a rise in the roasting temperature, but the rate of elimination of zinc does not increase; on the contrary, it falls in some cases, due, it seems, to the formation of zinc ferrite.

Next, the relation between the quantities of anthracite added, the roasting temperature, and the rate of elimination of lead and zinc when roasting for two hours is shown in Fig. 13. In this case the rates of elimination of lead and zinc are high according to the increase in the quantity of anthracite; that is to say, they are higher in the case of 5% than 3%. The best result is shown at a roasting temperature of 1100°C. At 1200°C, as the roasting temperature was too high, the sample became firmly sintered and so prevented volatilization of the lead and zinc. Comparing this result with the previous case of roasting for four hours, at 1100°C the result is better for two hours than four hours roasting at 1000°C. There is no difference in the rate of elimination of lead, but the rate of elimination of zinc is noticeably worse in the case of two hours.

It has been reported that limestone, instead of coke, gave the best result according to experiments on the elimination of lead and zinc from ferro-manganese ore by volatilization methods carried out at Utah University in the U.S.A. We thought that CaCO_s was perhaps decomposed by heat at 880°C more or less and rapidly generated







CaCO ₃ ≓	$CaO + CO_2$	$BaCO_3 \rightleftharpoons BaO + CO_2$		$CaSO_4 \gtrsim CaO + SO_3$		MgSO ₄ ₹	$MgO+SO_3$
Temperature (°C)	Pressure (mm Hg)	Temperature (°C)	Pressure (mm Hg)	Temperature (°C)	Pressure (mm Hg)	Temperature (°C)	Pressure (mm Hg)
700	31.4	1,017	5	700	11.5	1,100	345.0
800	208.0	1,097	120	800	38.0	I,I.:0	446.3
882	760.0	1,157	340	900	291.0	1,150	760.0
900	992.0	1,197	675	1,000	1,441.0	1,155	0.018
1,000	3,576.0						

 Table VII.

 Pressures of Thermal Decomposition of Carbonate and Sulphate.

 CO_2 which prevented the sintering of the sample and drove away the volatilization vapours of lead and zinc. Therefore 5% of CaCO₃ was added in the case of experiments No. 21-24. The result was almost the same as in the case without CaCO₃, that is to say, the volatilization loss of lead decreased and that of zinc slightly increased.

As the decomposition temperature of limestone showed a tendency to be much too low compared with the volatilization temperatures of lead and zinc, 5% of BaCO_s, which has a decomposition temperature of about 1200°C, was next added, and gave the results shown by the tests No. 25-30. These results compared with the results when using anthracite only are shown in Fig. 13. There is no great difference in the rate of elimination of lead, but that of zinc is markedly raised. The rate of elimination of léad and zinc together reaches over 90% when roasting for two hours at 1100°C with 5% of BaCO_s and 5% of anthracite. In all cases elimination rates of over 90% for lead and zinc are easily attained by roasting at 1200°C. In the case without BaCO₃ excess of sintering occurred at 1200°C to lower the result. On the other hand, in the case with BaCO₈ the interesting fact came to light that the rate of elimination was raised more and more by roasting to 1200°C. It can be said that good results were generally gained by the addition of $BaCO_3$.

Lastly, CaSO₄ and MgSO₄, which have intermediate decomposition temperatures, were added instead of BaCO₃ for the purpose of experiments. CaCO_s and BaCO_s have respectively, as mentioned above, decomposition temperatures of 882°C and about 1200°C, compared with which CaSO4 has a decomposition temperature between 900 and 1000°C and MgSO4 one of 1150°C. Volatilization experiments were therefore made with CaSO₄ and MgSO₄, but the rate of elimination of lead and zinc together was poor, and 0.78% of SO4 was still left in the sample at 1200°C. The result showed that 83-78% of SO_4 was decomposed. In a word, the volatiziation experiments with both CaSO4 and MgSO₄ gave bad results.

Conclusions.

We summarize below the conclusions arrived at from a study of the results of the above sintering and volatilizing experiments.

(1) The ferro-manganese ore produced from Kemaman does not melt at 1250° C in an oxidizing atmosphere, but it melts on heating for a short time at 1250° C in a reducing atmosphere in the presence of carbonaceous fuel.

(2) The above ferro-manganese ore is firmly sintered by heating at 1200°C with or without carbonaceous fuel.

(3) The rates of elimination of lead and zinc are increased, and the degree of sintering is generally raised, by increasing the quantity of anthracite added.

(4) In general, lead is easily eliminated by volatilization, but zinc with comparative difficulty.

(5) The rates of elimination of lead and zinc can respectively reach 98.7% and 82.5%, and the contents of lead and zinc can be respectively lowered to 0.1% Pb and 0.4% Zn, by roasting for two hours at 1100°C with 5% of anthracite.

(6) The rates of elimination of lead and zinc can together reach 91-96.5%, and the contents of lead and zinc can together be lowered to 0.1-0.2% by roasting at 1100° and 1200° C respectively with 5% of anthracite and 5% of BaCO₃.

(7) In the elimination of lead and zinc from ferro-manganese ore by volatilization we think that, as the actual operation, the following method is the best. Not less than 5% of anthracite or powdered coke should be added, and the roasting should be done in a long rotary kiln. The added carbonaceous fuel should burn well before reaching the discharge end, at the lower part of which heating in a reducing atmosphere should take place at a temperature of 1200° to 1250° C, high enough to sinter the material firmly but not to melt it.

This investigation owes much to Mr. Shinichi Sato and Mr. Jiro Wakasugi, assistants in the College of Ore Dressing, to whom we tender thanks.