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## Production of manganese ferroalloys from rich high-basidity ores

For the majority of manganese ores exported by world producers, low basicity (lower than 0,5) is typical, making it possible to produce ferrosilicomanganese from them in one stage by a slag process.

It is known [1, 2] that there are large deposits of manganese ores with high basicity in some solid ores. Chemical composition of such ores is given in Table 1.

Ore basicity varies within 0.76–2.93, which is, accordingly, 1.5–6.0 times higher the acceptable limit of basicity for ores, delivered for production of ferrosilicomanganese using a slag method. This implies that only carbon ferromanganese should be produced from these ores.

Production of carbonic ferromanganese using a flux method based on low-basic (acid) ores is quite completely covered in the literature [3, 4, 5] and is well mastered by process engineers.

### *Production of carbonic ferromanganese from high-basidity ores*

According to references [3], increased lime content in slags of carbonic ferromanganese increases their melting point, resulting in hearth temperature increase and improvement of manganese reduction conditions.

The author takes manganese oxide (MnO) content in the final slag as a parameter of reduction completeness. According to an almost linear approximation of the relation

$$MnO = \varphi \left( \frac{CaO + MgO}{SiO_2} \right).$$

A.D. Kramorov comes to the following properties:

B	1.2	1.4	1.6	1.8
(MnO)%	13.6	11.2	9.4	7.9

In the work [4] the following information is given about the basicity influence on slag melting point:

B	1.32	1.52	1.71
T <sub>melt</sub> , °C	1400	1490	1600

In the same document it is shown that enthalpy of manganese reduction from monoxide silicate is 17% higher if limestone is added for monosilicate formation compared to orthosilicate formation.

Thus, from the point of view of maximum reduction of manganese, increase of ore-flux mixture basicity to 3,0 and, as a result, increase of slag melting temperature, are advantageous.

For the purpose of technical and economical assessment of efficiency, the factor of manganese recovery into alloy is the main parameter, which is always lower than the reduction degree. The matter is a substantial share of reduced manganese is lost as steam in the off-gas phase.

In contrast to iron and chrome, manganese features high vapour pressure. The vapour pressure of pure manganese increases from 25 mm hg at 1450 °C to 100 mm hg at 1560 °C and to 330 mm hg at 1750 °C. In manganese compounds with iron and carbon, its vapour pressure is considerably lower and reaches 15–20 mm hg at carbon content of 4.0 % and temperature of 1500 °C. It is evident that increase of temperature of melting and overheating of slag and ally will promote further intensive manganese escape.

In order to reach maximum manganese recovery into the alloy produced from low-basic ores (concentrates,) in [3, 4, 5] it is recommended to maintain basicity of ore-flux part of charge within 1.1–1.4.

In [6] the practical maximum of manganese recovery was reached at B = 1.1. The authors explain further sharp decrease of manganese recovery in proportion to basicity increase to 1.2 by its losses for evaporation. At maximum manganese recovery (80 %), the highest silicon concentration (8.5 %) in ferromanganese was reached with minimum manganese monoxide content in slag.

In the paper [3] the following manganese distribution was obtained during ferromanganese melting from rich ores, %: to alloy – 80, to slag 8–10, to escape 10–12.

In the paper [5], based on the results of a thermodynamical analysis and tests, it is recommended to increase basicity to 1.6.

In practice carbonic ferromanganese production based on low-basic ores, the basicity of ore-flux part of charge and agglomerate can be easily increased to the rational values.

In case of rich ores of high (over 2,0) natural basicity, its decrease to the recommended 1.1 – 1.6 can be obtained by adding quartzite into charge. This method will inevitably result in a sharp increase of slag factors, and, as a result, to increased specific energy consumption and decreased manganese recovery into the alloy.

Some forecasts regarding efficiency of flux-free processing of high-basidity ores can be made on the basis of analysing the main quality criteria and the most important physical and chemical properties.

**Table 1. Averaged composition of manganese ores of world exporters**

Item	Manufacturer country	Chemical composition of manganese ores, %% of dry weight										
		Mn	Fe	$\frac{Mn}{Fe}$	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	P	CaO	BaO	K <sub>2</sub> O	MgO	Na <sub>2</sub> O
1	Kazakhstan, oxide concentrate, 1 grade, Zhairam [2]	35.9	3.86	9.30	5.2	1.30	0.076	14.8	-	-	0.43	-
2	Kazakhstan, oxide-carbonate concentrate, 2 grade, Zhairam [2]	30.0	12.33	2.43	5.01	2.00	0.082	13.9	-	-	0.60	-
3	Kazakhstan, oxide-carbonate concentrate, 1 grade, Dzhezdinsk [2]	37.6	10.55	3.56	8.91	1.11	0.073	9.6	-	-	0.88	-
4	Brazil [2]	47.5	6.70	7.1	3.65	8.10	0.10	0.23	2.23	1.35	0.30	0.08
5	RSA, oxide concentrate, 1 grade [3]	47.2	11.9	4.00	5.65	0.37	0.04	6.0	0.4	0.10	0.80	0.10
6	RSA, oxide-carbonate concentrate, 2 grade (Kalahari) [3]	38.0	4.9	7.76	6.00	0.20	0.02	13.5	-	0.10	3.60	0.10

The methods and the scope of changing quality criteria for manganese ores are given and substantiated in our article [7]. The only change was about point 5 (evaluation of process preference by criteria SiO<sub>2</sub>/MnO). The reverse order of grades is accepted here (from 1 at SiO<sub>2</sub>/MnO ≥ 0.4 to 3.0 at SiO<sub>2</sub>/MnO ≤ 0.25), since all ores with B > 0.5 basicity should be directed for production of carbonic ferromanganese only.

Concentrate quality criteria values are summarised in Table 2.

When analysing ore quality criteria values, it can be seen that ores No 2 and 3 are not suitable for melting standard alloy grades, containing at least 65 % manganese, up to 6 % silicon and 7% carbon. In order to produce such alloy, the ratio in the source ore should be more than 4.

Ores with high iron content, in which the Mn/Fe ratio is < 4, should be used as charge-adjusting material for ores with a high Mn/Fe ratio. In particular, ores No 2 and 3 can be added to ore No 1 (Mn/Fe=9.3) in the amount ensuring the following in the alloy: 70–82 % Mn, 1.5–2.0 % silicon and up to 8 % carbon. In terms of P/Mn criterion, concentrates of ores No 5 and 6 are related to low-phosphorus ores, the rest being medium-phosphorous. From this point of view, low-phosphorous concentrates are precious ingredients for mixing with high-phosphorous ones in the charge, including low-basic ores, in the proportions ensuring standard phosphorus content in alloys. Concentrates No 5 and 6 got the highest grades, with No 1 and 4 being average and No 2 and 3 of low grades. The low grade scores were because of low val-

**Table 2. High-basicity concentrate quality criteria values and their evaluation in grades.**

Item	Manufacturing country	Content of Mn, %	Grade	$\frac{Mn}{Fe}$	Grade	$\frac{P}{Mn} \cdot 10^{-3}$	Grade	Basicity, B	Grade	$\frac{SiO_2}{MnO}$
1	Kazakhstan, oxide concentrate, 1 grade, Zhairam [2]	35.9	3	9.30	2	2.1	2	2.93	3	0.11
2	Kazakhstan, oxide-carbonate concentrate, 2 grade, Zhairam [2]	30.0	2	2.43	1	2.7	2	2.90	3	0.13
3	Kazakhstan, oxide-carbonate concentrate, 1 grade, Dzhezdinsk [2]	37.6	3	3.56	1	1.9	2	1.18	3	0.18
4	Brazil [2]	47.5	3	7.10	2	2.1	2	0.76	2	0.06
5	RSA, oxide concentrate, 1 grade [3]	47.2	3	4.00	1	0.8	3	1.30	3	0.10
6	RSA, oxide-carbonate concentrate, 2 grade (Kalahari) [3]	38.0	3	7.80	2	0.5	3	2.85	3	0.12

LOI	Working mass moisture	B, basicity
3.23	0.23	2.93
12.30	0.50	2.90
8.91	0.40	1.18
-	8.00	0.76
4.00	2.00	1.27
12.00	2.00	2.85

ues of Mn/Fe (2.43 and 3.56, accordingly) and increased phosphorus proportion.

The following physical and chemical properties of ores (concentrates) are considered important from the process point of view:

- loss in weight due to moisture removal and decomposition of Mn, Mg and Ca carbonates within the temperature range of 550 to 950 °C;
- changes in structural strength and porosity of ore lumps at t=600–850 °C;
- softening and melting temperature;
- ore and charge shrinkage factors;
- changes in specific electrical resistivity of ores

with temperature increase.

Within the temperature interval of 550–950 °C, the highest loss in weight is observed for ore samples with high carbonates content (No 2, 3 and 6).

In particular, the total loss in weight of RSA ore sample (No 6) was 14 %.

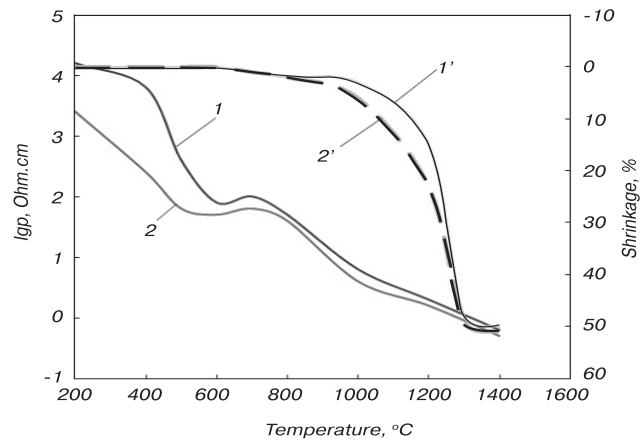
The breakdown of structural strength because of a thermal shock at 750 °C is observed the most clearly for high-basic, high-carbonate ores (No 2, 3 and 6).

In particular, for ores No 2 and 6 delamination of lumps along the planes was observed with pronounced increased content of magnesium and calcium carbonates. Along with that, initial porosity of 8–10 % was increased by 2.5–3.0 times.

Grade	Σ grades
2	12
2	10
2	11
3	12
3	13
3	14

The latter fact is favourable for reductibility of these ores thanks to development of chemisorption of carbon monoxide on delamination surfaces. Here we will note that decarbonisation of high-basic ores in charge at the expense of off-gas heat results in noticeable concentration increase of the target (Mn, Fe, Si) elements and accompanying minerals. Some ore weight loss is associated with the reduction reactions of higher oxides of manganese and iron to the lower ones ( $Me_2O_3 \rightarrow Me_3O_4 \rightarrow MeO$ ) because of participation of carbon monoxide and off-gas hydrogen in them.

Influence of temperature on specific electric resistivity and shrinkage can be evaluated by the curves in Fig. 1, where curves 1 and 1' describe the changes of carbonic ferromanganese charge properties, the ore part of which



**Fig.1. Temperature relation of carbon ferromanganese burden from shrinkage (% of layer height) and specific electric resistance logarithm ( $\rho$ , Ohm-cm). Curves 1 and 1' – reflect specific electric resistance and layer shrinkage of carbon ferromanganese burden formed by acid ferromanganese ore and flux (B-0,7), curves 2 and 2', correspondingly, burden behavior formed by high-basicity manganese (B-2,6) (table 2)**

consists of low-basic ore (0,3) and lime of technical purity with a view of 1,6 basicity. Curves 2 and 2' correspond to specific electrical resistivity and shrinkage of charge, the ore part of which consists only of ore of 2,8 basicity.

Within the temperature range of 200-820 °C (before softening), a sharp decrease of electric resistivity of both charges is observed with the material volumes being the same. This demonstrates that removal of oxygen and moisture from lattices of psilomelane, braunite, hausmannite, and further of carbon dioxide from manganocalcite does not hamper structural strength of these minerals.

Decreased electric resistivity within the specified temperature range is consistent with  $\rho$  decrease, typical for carbonic part of charge. It is natural, that temperature reconstruction of mineral component lattices exerts the same influence on changes of charge  $\rho$ .

The sharp decrease of charge volume takes place from the beginning of softening to the moment of formation of polyoxide melt, containing lower oxides of manganese and iron. Melting temperature for both samples is within 1260-1280 °C. Compared to charge 1, for charge 2 (high-basic concentrate) lower electric resistivity values and earlier volume reduction (shrinkage) are typical. Probably, these facts are associated with increased concentrate (2) density, and, accordingly, with the increased relation of volumes of carbonic and ore parts compared to a relatively more “incoherent” mass of charge 1. One can assume that formation and further melting of silicates of calcium, manganocalcite, rhodonite and bustamite from ore and lime minerals requires higher temperatures compared to naturally-formed mineral structure of high-basic ore. Hence it follows that formation of polyoxide melt (primary slag) from charge 2 is more energy-efficient compared to charge 1.

The laboratory tests in Tamman furnace (small laboratory furnace of electric resistance. – comm.auth.) for pro-

ducing carbon ferromanganese from high-basic ores demonstrated that at  $t = 1480\text{ }^{\circ}\text{C}$  and  $\tau = 40$  minutes, recovery of manganese plus iron is 85 %, that of silica – 18 %; there is 8 % of manganese in slag, escape losses are 7 %.

The alloy was of the following composition:

Mn = 75–80 %, Si = 0.8–1.2 %, C = 7–7.2 %, P = 0.08–0.10 %.

An industrial test of producing carbon ferromanganese demonstrated that in order to decrease manganese losses with the gas phase it is necessary to increase surface area of the carbonic part of charge in every possible way, including reducing agents – rippers (briquetted peat, lignine, saw dust etc.).

### *Slag-less production of ferrosilicomanganese*

Feasibility of industrial FeSiMn production using a two-stage slag-less method was mentioned already at an early stage of establishing the domestic ferroalloy industry [3].

At that time, abundance of manganese raw materials in the USSR (Georgia, Ukraine, the Urals) with low basicity ( $B < 0,5$ ) contributed to industrial development of the only rational one-stage slag method of FeSiMn production.

The slag-less method of producing high-silica alloys (25–90 % FeSi, 48 % ferrochrome silicon) is widely used in ferroalloys plants.

The process main point is in the reaction of silica reduction by carbon of reducing agents with addition of a metal phase (Me):



In the first case (FeSi), steel cuttings are added into the charge, in the second one (FeSiCr) carbon ferrochrome is added. For FeSiMn production it is necessary to introduce carbon ferromanganese.

It is known that silica recovery factor is decreased in proportion to increase of its concentration in the final alloy. In particular, when melting ferrosilicon from 18–45 % Si  $K_{\text{rec}} = 98.5\%$ , with production of 75 %  $K_{\text{rec}} = 92\%$  [9].

Evidently, recovery allowance should be made when calculating composition of silicomanganese, containing over 45 % silica.

It is known that increased silica concentration in ferrosilicomanganese leads to reduced concentration of carbon and phosphorus.

When using a slag method, increased silica content over 25 % is associated with considerable material and energy

costs, hence, possibilities of further decrease of carbon and phosphorus in the alloy are limited. Inapplicability of process ferrosilicomanganese for producing low- and ultralow-carbon and almost phosphorus-free grades of ferromanganese is a direct consequence of this limitation.

The slag-less method removes these limitations, since silica concentration in the alloy can be increased to any rational values (30–75 %).

### *Conclusion*

Production of manganese alloys from high-basic ores is efficient from the technical and economical point of view, if the processes of reduction and refinement in terms of carbon and phosphorus are implemented in three stages:

In the first stage, saleable and process carbon ferromanganese should be produced;

In the second stage, saleable and process ferrosilicomanganese should be produced using a slag-less method;

In the third stage, by mixing ore-lime melt with liquid ferrosilicomanganese (17–65% Si), all grades of ferromanganese should be produced (from medium- to low-carbon low-phosphorus products).

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