UTILIZATION OF SUBSTANDARD AND OFFGRADE RAW MATERIALS FOR CHROMIUM AND MANGANESE FERRO-ALLOYS PRODUCTION

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ABSTRACT

Chromium and manganese ferro-alloys are widely used in steel industry. The amount of rich mineral raw materials for ferro-alloys decreases from year to year while several countries including Russia have reserves of low-grade hard-cleaning ores. The main advantage of such raw materials is the price for tonne - percent of element (Cr, Mn), which is lower than for high-quality raw materials.

Mineral raw materials account for a considerable part of ferro-alloy price. So, the use of low-priced substandard raw materials can compensate high process costs. In practice, problems of concentration and its cost (including stages of sintering or nodulizing) led to charging ferro-alloy furnaces with a mixture of rich and poor ores.

Poor ores can be applied for manufacturing alloys with low chromium and manganese contents, for example, high-carbon chromium alloys with low chromium - the so called "Charge chrome", complex and charge (ferro-chromium silicon and ferro-manganese silicon alloys) ferro-alloys that used for refining processes.

As was revealed by several studies, characteristics of substandard and complex ferro-alloys when used for deoxidation and alloying, are highly competitive in comparison with standard ones.

Common use of poor ores can revive a number of Russian ore deposits not used before. New types of raw materials (especially poor in the basic elements) must get a reliable metallurgical estimation since ores with even a small difference of contents can greatly change engineering-and-economical performance.

Approach to a metallurgical estimation of manganese raw materials (a combination of calculations and experimental data) was developed by the authors.

So, the involvement of poor chromium and manganese ores into industrial process requires a development of new comprehensive approach which includes a complete estimation of metallurgical characteristics of mineral raw materials and produced substandard and complex ferro-alloys. This approach will provide a development of new competitive technologies of ferro-alloy production. Some examples of development and application of technological solutions are given.

1 FERRO-ALLOY PRODUCTION STRUCTURE AND MINERAL RESOURCES

Manganese and chromium ferro-alloys are industry-leading (fig. 1). So, the problem of chromites and manganese ores is the issue of the day for ferro-alloy producers.

1.1 Chromites

Chromites resources are found in 67 countries and in 61 of them estimated at 15.9 billion ton (table 1).

Chromites of Kimpersai ore deposit in Kazakhstan were the traditional source of raw materials for Russian ferro-alloy producers during decades.

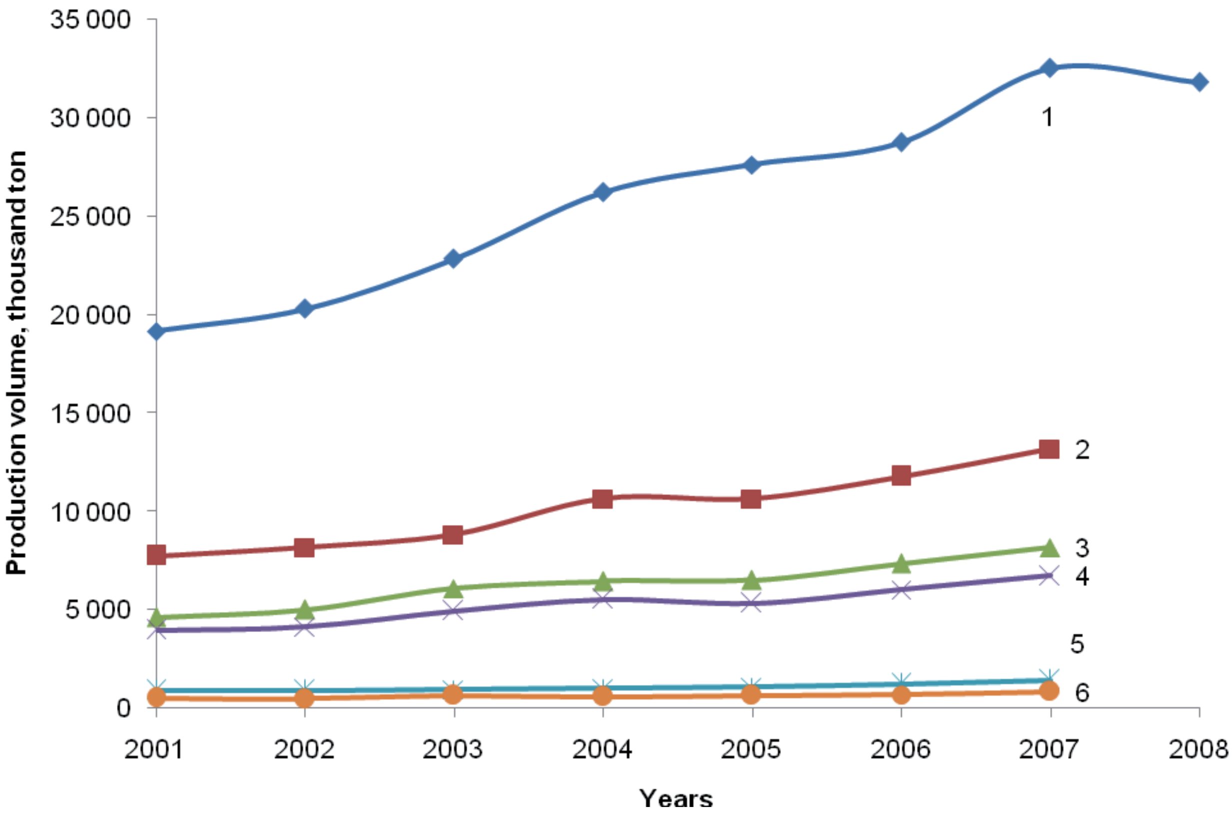

Figure 1: World ferro-alloy production volume in 2001 – 2008. 1 – total volume; 2 – manganese alloys; 3 – ferrochromium; 4 – ferrosilicon; 5 – iron nickel; 6 – silicon.

Russian reserves of chromites are comparatively small and estimated at 15 million ton. Established resources are estimated at 9.5 million ton, and 5.4 of them are concentrated in Saranovskoe deposit in Perm region.
Commercially significant chromites must contain more that 40% of Cr_2O_3 and ratio of Cr_2O_3:FeO more than 2,5 [2] according to industrial requirements.

Table 1: World resources and reserves of chromites, in million ton and average content of Cr_2O_3 [1].

Country	Reserves, mt	Established resources	World proportion, %	Content of Cr_2O_3, %
Russia	486	9.5	0.37	30.5
Finland	165	50	1.97	26.0
Kazakhstan	1316	317.6	12.5	50.2
Zimbabwe	986	143	5.6	43.2
South African Republic	11748	1780	70.1	37.0
Brazil	71.9	32.9	1.3	22.3
USA	337.5	2.5	0.1	11.5
Greenland	169	0	0	21.0
Total	15937.5	2541.0	100	

1.2 Manganese ores

The most of manganese is produced in the form of ferro-alloys, and their specific consumption per ton of steel gradually increases.

Data on reserves and established resources of manganese ores of 10 main countries producers and average manganese content on 01 January 2003 [2] are given in table 2.

Table 2: Resources of manganese ores, million ton and average Mn content, %.

Country	Reserves, mt	World proportion,	Established resources	World proportion, %	Content of Mn, %
Ukraine	2411	15.9	2242	42.6	23
	9000	59.4	1040	19.8	45
Kazakhstan	600	4	426	8.1	20
Gabon	376	2.5	236	4.5	50
Georgia	247	1.6	223	4.2	20
Brazil	340	2.2	174	3.3	41
Russia	157	1	149	2.8	20
China	325	2.1	130	2.5	23
Australia	213	1.4	128	2.4	41
Bulgaria	180	1.2	126	2.4	27
World	15140	100	5260	100	-

Probable reserves of manganese ores in Russia are estimated at 841 million ton, and 243 million ton of them are inferred. Most of them are concentrated in Siberia and the far East. About three quarters of all probable reserves of Russia are oxide ores.

Quality of Russian manganese ores is poor. The main part of explored reserves is carbonate hard-cleaning ores with average manganese content of 20%. Most of manganese ore deposits are small.

At present time ferro-alloy producers all over the world face the deficit of quality ores (quality of both chemical and granulometric composition).

2 INVOLVEMENT OF POOR CHROMITES AND MANGANESE ORES INTO FERRO-ALLOY PRODUCTION CYCLE

2.1 Common ways of involvement of poor ores into production cycle

Annually gap in demand for chromium and manganese ferroalloys and diminishing resources of rich ores is increasing. So, the involvement of poor chromites and manganese ores into technological process is becoming inevitable both in Russia and World.

The most common practice in ferro-alloy industry is use of rich and poor ores mixtures in submerged electric arc furnaces.

Besides, it is rational to use poor ores and concentrates for production of manganese- and chrome-bearing alloys for steel treatment and further refining [1]. Candidate alloys are:

- commercial high-carbon ferromanganese and ferrochromium with low (off-grade) content of main element (Cr, Mn);
- complex manganese- and chrome-bearing ferro-alloys with additional (optional) elements for treatment of different steel grades (silicon, titanium, vanadium and other);
- foundry alloys, e.g. foundry ferrochromium, ferrochromium silicon used at refining processes.

There are enough working examples of poor ores use for production of chrome- and manganese-bearing ferro-alloys.

Many foreign ferro-alloy plants use poor chromites for production of high-carbon ferrochrome with low (off-grade) content of chromium, i.e. so called “charge chrome”. Technology of “charge-chrome” allows extending national sources of raw materials by using chromites with low ration of Cr/Fe.

Poor chromites and manganese ores were used for production of complex ferro-alloys, such as Fe-Cr-Mn-Si (ferrochromium manganese silicon with ~ 40 % Cr, ~ 16 % Mn, ~ 12 % Si) and Fe-Cr-Mn-Si-Ca-Ti (with calcium and titanium).

Production of complex manganese- and chrome-bearing ferro-alloys can involve poor chromites and manganese ores into technological process and replace standard Cr, Mn and Si alloys by cheaper complex alloys with these elements.

Poor chromites of different small deposits in Chelyabinsk region were used for production of foundry high-carbon ferrochromium at JSC “Chelyabinsk electrometallurgical works” (“CHEMK”). The alloy contains, wt.%: 50-52 % Cr; ~ 5 % Si 5-6 % C. Ferrochromium was taken for production of foundry ferrochromium silicon (50 – 52 %Si), that was used as a reducing agent at smelting of rich imported chromites for production of commercial low-carbon ferrochromium (60% Cr) [3]. So, the portion of poor ores in raw material balance of “CHEMK” was increased by using this technological scheme of ferrochromium production.

2.2 General approach to poor ores use and related problems

2.2.1 Optimal ferro-alloy composition

New alloys are the result of involvement of poor ores into technological process. So, their potential for steel treatment needs an assessment.

The algorithm of application of optimal ferro-alloy composition was developed [4]. It includes:
- preliminary selection of alloy elements according to composition and properties of the treated metal;
- estimation of optimal proportions of elements on the basis of physic-chemical properties and characteristics of interaction with iron-carbon alloy.

These physic-chemical properties are: melting temperature, density, ferro-alloy oxidation rate, heat efficiency of ferro-alloy interaction with melt, melting rate of ferro-alloy when added to melt and others.

Dozens of ferro-alloy compositions were developed by using the algorithm of optimal ferro-alloy composition. The new alloys are better and faster absorbed by steel melt, having less detrimental impurities and better effect on metal properties.

2.2.2. Metallurgical estimation of ores and concentrates

When choosing new ores and concentrates (especially poor) it is necessary to make a reliable metallurgical estimation. It is related with difference in quality and price of raw materials affecting the performance characteristics of ferro-alloy production.

We propose [5] a rational approach to metallurgical estimation of raw materials (by the example of manganese ores), that includes preliminary calculations based on chemical composition and statistic method for determination of reduction ratio (for similar types of ores); thermodynamic modeling of carbothermic reduction of manganese; technological calculations of charge and specific energy consumption. In addition, the detailed estimation based on experimental data is made, which includes investigation of softening temperatures and specific electric resistance of concentrates.

Combined influence of these characteristics must be established by complex rating estimation. For this estimation of factors contribution to total characteristic of raw materials we used four quality indices: K_R, K_{SEC}, K_S and K_{SER} for manganese reduction ratio, specific energy consumption, softening temperatures and specific electric resistance.
Value of indices K_R, K_{SEC}, K_S and K_{SER} differed from 0 to 1 (for the best value of every characteristic). A summary metallurgical characteristic of concentrate estimated as

$$K_{OV} = K_R + K_{SEC} + K_S + K_{SER} \quad (1)$$

where: K_R – manganese reduction ratio index;
K_{SEC} – specific energy consumption index;
K_S – softening temperatures index and
K_{SER} – specific electric resistance index.

For calculation of quality indices of different ores and concentrates we took as 1:

- maximum reduction ratio of manganese for high-carbon ferromanganese and ferro-manganese silicon;
- minimum specific energy consumption for high-carbon ferromanganese and ferro-manganese silicon;
- maximum softening temperatures;
- maximum specific electric resistance;
- minimum temperature interval of softening.

When studying problem of quality of manganese ores and concentrates it is important to take into consideration content of phosphorus. It is proposed to use ratio of phosphorus to manganese in concentrate, (taking into account thermodynamically calculated manganese reduction ratio and phosphorus reduction ratio 85%) for estimation of different manganese raw materials.

Poor manganese ores usually have low manganese reduction ratio index and high specific energy consumption. Experimental data on softening temperatures and specific electric resistance of different concentrates vary greatly and can't be calculated. Phosphorus content affects on final estimation result from the point of view of quality of alloy but it doesn't influence on the process smelting or reduction.

All these characteristics allow estimating raw material on the basis of physic-chemical characteristics of ores and concentrates allow comparing them more precisely in laboratory without industrial melts.

3 CONCLUSION

So, the involvement of poor chromites and manganese ores is inevitable for solution of raw materials problem of ferro-alloy plants. At the present time ferro-alloy producers have to use mixtures of rich and poor ores for submerged arc furnaces.

Production of manganese- and chrome-bearing ferro-alloys (suitable for steel treatment or further refining) from poor ores and concentrates is a rational approach to a problem of raw material quality. It will extend list of sources of raw materials by involving proved off-grade ore deposits that haven't had industrial application. Moreover, there won't be a need of sufficient investments for exploration work.

To select the ferro-alloy type and suitable raw materials it is necessary to use approach of physic-chemical characteristics estimation for both the alloy and ores.

4 REFERENCES

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