

# Quality Assessment Method for Chromite Sand to Reduce the Number of Cast Steel Surface Defects

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# Abstract

This paper discusses the ability to apply the test method using a scanning electron microscope (SEM) together with EDS (Energy Dispersive Spectroscopy) analysis to assess the quality of fresh chromite sand delivered by various suppliers to Huta Małapanew Sp. z o.o. The research was initiated due to the non-cyclical occurrence of surface casting defects, i.e. pitted skin and burn-on of chromite moulding sand for cast steel casting. The scope of studies comprised the quality assessment of sixteen chromite sand batches delivered for six months by two suppliers. The analysis of the results obtained was used to describe components of the tested chromite sand batches and develop criteria for their quality assessment, considering the chemical composition of chromite grains and the amount of impurities in the form of silica sand and the binder particles. Moreover, clear suggestions were developed concerning the ability to use the given chromite sand batch as the base of moulding sand made in Alphaset technology in Huta Małapanew Sp. z o.o.

Keywords: Moulding sand, Chroimite sand, Casting defects, Cast steel, SEM, EDS

# 1. Introduction

Chromite sand is considered to be the second, following silica one, material used most often as a moulding sand matrix in the foundry industry. This stems from specific performance properties of chromite sand, i.e. high melting and sintering temperature as well as relatively low thermal expansion with high thermal conductivity coefficient [1, 2].

The chromite sand properties presented in Table 1, much higher than those for silica sand, explain its use as the matrix of moulding sand types dedicated to demanding alloys, i.e. nonalloy, and primarily, alloy cast steel resistant to corrosion, abrasion and heat [1-5]. Moreover, chromite sand is also used currently for moulding sand types dedicated to grey cast iron, which is difficult in terms of technology, with flake or nodular graphite [1, 2, 6-9].

However, usually, due to high price of fresh chromite sand, several times higher than that of silica sand per tonne, the moulding sand based on it for cast steel and cast iron castings is usually limited to facing sand, whereas the backing sand is based on silica sand or regenerated chromite sand. Another solution, also aimed at reducing process costs and improved cast quality, is to use chromite sand locally in the mould where it reduces temperature because of its high thermal conductivity coefficient. An example of a local use of sand based on chromite combined



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#### Table 1.

Selected properties of chromite and silica sand as a moulding sand matrix, important for foundry engineering

	Sand			
Property	Silica sand	Chromite sand	References	
Density, g/cm <sup>3</sup>	2,65	4,50	[1, 2, 11, 13]	
Bulk density, g/cm <sup>3</sup>	1,40÷1,60	2,60÷2,80	[1, 2, 5, 11]	
Melting point, °C	1680÷1710	1850÷2000	[1, 2, 11, 13]	
Sintering temperature, °C	1350÷1400	1350÷1500	[1, 2, 12]	
Succific heat	0,70 in 20°C 0,55 in 20°C			
Specific field,	1,30 in	0,95 in	[7]	
J/(g⋅K)	900°C	900°C		
Thermal	1,55 in	0,65 in	[1, 2, 8,	
expansion, %	900°C	900°C	10, 13]	
Thermal conductivity	0,6 in 20°C 0,8 in 20°C		[7]	
coefficient, W/(m·K)	0,9 in 900°C 1,3 in 900°C		[']	
Average solidification	350 for a casting wall thickness of 10mm	150 for a casting wall thickness of 10mm	[7]	
time of grey cast iron, s	800 for a casting wall thickness of 20mm	350 for a casting wall thickness of 20mm	[/]	
Chemical nature	Slightly acidic (6,8÷7,0 pH)	Alkaline (7,0÷10,0 pH)	[1, 5, 11]	
Resistance to liquid alloy penetration	Average	Very good	[1, 2]	

Generally speaking, sand based on chromite guarantees higher quality of the casting surface when compared to the one based on silica sand. For example, Figure 1 presents surface of railway infrastructure components, i.e. Insert R300 frogs, made from manganese cast steel in Huta Małapanew Sp. z o.o. The use of sand based on chromite, contrary to the one based on silica sand, allows to prevent such surface defects as sand burn-on to the cast, in particular in the running part of the cast difficult to clean using machining methods.

However, due to the chromite sand mining from various deposits located primarily in South Africa (ca. 70% of global resources) and, to a lower extent, in Zimbabwe, Finland and post-Soviet Union countries [14, 15], with the absence of its rinsing process, some delivered batches do not have sufficient purity and are characterised by the lower content of the basic ingredient, i.e.

Cr oxide, with excess impurities in the form of silica sand grains and the binder, i.e. small fractions, below 0,02 mm. Moreover, excessive amounts of Ca, Al and Mg oxides are considered chromite sand pollutants. Acceptable content of the said ingredients, as per PN-H-11007:1991 standard, is presented in Table 2.



Fig. 1. A view of the running part of Insert R300 frog (net mass 273 kg) cast from manganese cast steel in Huta Małapanew Sp. z o.o. 1 – when moulding sand based on chromite sand in Alphaset technology was used; 2 – when sand based on quartz sand in Alphaset technology was used

Table 2.

Requirements	concerning	chromite	sand	chemical	composition
according to P	N-H-11007:	1991			

Components content, wt.%		
Cr <sub>2</sub> O <sub>3</sub>	≥ 46,0	
Fe <sub>2</sub> O <sub>3</sub>	≤ 26,0	
Al <sub>2</sub> O <sub>3</sub>	≤ 15,0	
MgO	≤ 10,0	
SiO <sub>2</sub>	≤ 1,5	
CaO	$\leq 0,1$	

According to data in [1, 4, 5, 16], the highest threat for the chromite sand quality and, consequently, for the quality of casting made in sand based on it is, on the one hand, excessive binder content which generates surface defects related to gas, i.e. skin pitting, and on the other, addition of silica sand resulting in sand burn-on to the cast surface. Excessive amount of SiO2 promotes penetration of liquid alloy, e.g. cast steel, inside the sand mould and, consequently, is accountable for burn-on on castings and formation of sand buckles, based on the mechanism described in [5, 16]. In oxidative conditions accompanying the process of pouring liquid alloy in the mould, liquid iron oxide forms on its surface which, reacting with SiO2 in the moulding sand, creates liquid iron orthosilicate, the so-called fayalite. This is how silica sand grains are melted by the liquid alloy. Consequently, voids in the intergranular spaces are formed in the top layer of the mould cavity and are penetrated by the liquid alloy which, once solidified, creates burn-on particularly difficult to remove due to their high content of hard phases, i.e. fayalite and glassy phase. To reduce occurrence of the above-mentioned cast defects from sand, protective coatings can be applied on the mould cavity



and/or chromite sand quality can be tested primarily in terms of the content of a binder and silica sand.

In the paper [6], it was proposed to assess the binder content in chromite sand by means of a modified method of dusty fraction washing by placing sand sample in 3% aqueous solution of NaOH. This method allows to separate and then determine the share by weight of both free binder particles and, as a result of NaOH use, also those separated from chromite grains. The analysis of the test results revealed that the maximum value allowing to prevent skin pitting is the binder content not exceeding 0,4% by weight. Moreover, it was proved that the employed method for chromite sand quality assessment is effective, but also tedious and laborious.

The papers [17 and 18] describe the ability to determine SiO<sub>2</sub> content precisely in chromite sand using advanced testing methods, i.e. XRD (X-Ray Diffraction), XRF (X-Ray Fluorescence) and FTIR (Fourier Transform Infrared Spectroscopy).

Whereas, in this article, the quality of chromite sand delivered to Huta Małapanew Sp. z o.o. was assessed using a scanning electron microscopy (SEM) and EDS (Energy Dispersive Spectroscopy) analysis. The research was initiated due to the noncyclical occurrence of surface casting defects, i.e. pitted skin and sand burn-on made using Alphaset technology based on chromite sand for steel casting in Huta Małapanew Sp. z o.o. Based on the reference works review presented in this paper, a hypothesis was adopted that the occurrence of the above-mentioned casting surface defects results from chromite sand impurity with excess amount of silica sand and/or the binder although the presence of such impurities in the non-acceptable amount is not found by means of analysing the certificates of the chemical composition of the tested chromite sand batches delivered by their respective suppliers.

### 2. Experimental procedure

The scope of tests comprised the analysis of sixteen chromite sand batches delivered to Huta Małapanew Sp. z o.o. for six months by two suppliers (Fig. 2). Based on the provided delivery certificates (Tab. 3), all the tested chromite sand batches met the requirements concerning the chemical composition and had other required properties, i.e. they contained  $Cr_2O_3 = 47.8 \div 48.5$  wt.%,  $Fe_2O_3 = 25.0 \div 26.3$  wt.%,  $Al_2O_3 = 14.8 \div 15.2$  wt.%, MgO = $9.7 \div 10.1$  wt.%, SiO<sub>2</sub> = 0.4 \div 0.5 wt.%, CaO = 0.1 \div 0.2 wt.%, MnO+Na<sub>2</sub>O+TiO<sub>2</sub> approx. to 1.0 wt.% with  $pH = 7.2 \div 8.0$ , their main fraction was 0.4/0.32/0.2 with the average grain size of 0.25÷0.35 mm, homogeneity degree of 84÷88% and the binder content of 0.0%. On the basis of the analysis of the provided certificates (Tab. 3), it is concluded that the studied chromite sands probably originated from two different ores.

Despite the correct chemical composition and other properties mentioned above shown in the applicable certificates, the use of chromite sand as moulding sand matrix made using Alphaset technology resulted in non-cyclical occurrence of surface casting defects, e.g. skin pitting and burn-on in steel castings made in Huta Małapanew Sp. z o.o., particularly in places which were not well available for the shot blasting process (Fig. 3).



Fig. 2. A view of an example of chromite sand delivered in the analysed period to Huta Małapanew Sp. z o.o.: a) supplier 1, b) supplier 2

Table 3.

Components content in the studied chromite sands according to certificates provided by suppliers

The chromite sand no. 1+5 from supplier 1			
Cr <sub>2</sub> O <sub>3</sub>	48.5 wt.%		
Fe <sub>2</sub> O <sub>3</sub>	25.0 wt.%		
Al <sub>2</sub> O <sub>3</sub>	15.2 wt.%		
MgO	9.7 wt.%		
SiO <sub>2</sub>	0.4 wt.%		
CaO	0.1 wt.%		
MnO, Na <sub>2</sub> O, TiO <sub>2</sub>	rest		
The chromite sand no. 6+10 from supplier 1			
Cr <sub>2</sub> O <sub>3</sub>	47.8 wt.%		
Fe <sub>2</sub> O <sub>3</sub>	25.9 wt.%		
Al <sub>2</sub> O <sub>3</sub>	14.8 wt.%		
MgO	9.8 wt.%		
SiO <sub>2</sub>	0.4 wt.%		
CaO	0.2 wt.%		
MnO, Na <sub>2</sub> O, TiO <sub>2</sub>	rest		
The chromite sand no	o. 1÷3 from supplier 2		
Cr <sub>2</sub> O <sub>3</sub>	48.3 wt.%		
Fe <sub>2</sub> O <sub>3</sub>	26.3 wt.%		
Al <sub>2</sub> O <sub>3</sub>	15.1 wt.%		
MgO	9.8 wt.%		
SiO <sub>2</sub>	0.4 wt.%		
CaO	0.1 wt.%		
The chromite sand no. 4+6 from supplier 2			
Cr <sub>2</sub> O <sub>3</sub>	48.5 wt.%		
Fe <sub>2</sub> O <sub>3</sub>	26.0 wt.%		
Al <sub>2</sub> O <sub>3</sub>	14.8 wt.%		
MgO	10.1 wt.%		
SiO <sub>2</sub>	0.5 wt.%		
CaO	0.1 wt.%		

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Consequently, to assess the quality of the said chromite sand, the test method using Phenom ProX scanning electron microscope (SEM) with backscattered electron (BSE) imaging and electron beam accelerating voltages of 10 and 15 kV, and with an energy X-ray dispersive spectrometer (EDS) was used. The tests were supported with observations of chromite sand samples using an optical camera (OC) with up to 100x magnification. For every tested chromite sand batch, a sample with the area of 36 mm<sup>2</sup> was taken, containing 1000 grains on average (Fig. 4). For the aim of the sample prepared a 6x6 mm graphite adhesive tape is used.



Fig. 3. A view of cast steel casting defects, i.e. burn-on of moulding sand based on chromite prepared in Alphaset technology in the case of a profile of a mining chain conveyor (net mass 415 kg) cast from unalloyed cast steel in Huta Małapanew Sp. z o.o.



Fig. 4. A view of an example of a chromite sand sample for tests using OC, SEM and EDS, mag. 40x

# 3. Results and discussion

Figures 5÷10 present the results of macro- and microscopic observations of characteristic grain components found in all analysed chromite sand samples. Based on their morphology and colour, three types of components were distinguished which were later divided into grain type A, B and C. To identify their chemical composition, EDS microanalysis was carried out for the grain types. Next, for each of the grain types, their impact on the chromite sand quality was analysed and individual assessment criteria were developed which served to decide clearly whether the chromite sand batch is usable as a base of moulding sand made using Alphaset technology in Huta Małapanew Sp. z o.o.

Figures 5 and 6 present an example of findings concerning the most abundant component of the analysed chromite sand batches, i.e. A grain type, as chromite grains containing Cr, Fe, Al, Mg, Si and O in various concentrations. For spot EDS analysis, twenty A type grains were selected randomly from each sand sample for which the concentrations in % by weight were averaged for Cr, Fe, Al, Mg, Si and O. The analysis of the reference data in [1, 2, 4, 5, 17 and 18] and the obtained results, the following acceptable maximum concentrations of the elements in A type grains were proposed and described as criterion K1:

- $Cr \ge 28.0$  wt.%,
- Fe  $\leq 20.0$  wt.%,
- $Al \le 8.0\%$  wt.%,
- $Mg \le 7.0$  wt.%,
- $Si \le 1.0$  wt.%,
- O = rest.

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Fig. 5. An example of a chromite grain marked as type A: a) SEM, mag. 240x, b) EDS spectrograph in spot 1



Fig. 6. An example of a chromite grain marked as type A: a) SEM, mag. 270x, b) EDS spectrograph in spot 2

Figures 7 and 8 present examples of results concerning impurities of the analysed chromite sand batches with silica sand grains marked as type B. It was found out that, despite the morphology of the silica sand grains similar to the chromite sand grains, their different colour allows to carry out qualitative analysis of SiO<sub>2</sub> based on macroscopic observations which is presented in Figure 8. Based on the guidelines in Table 2, reference data analyses [1–5, 9, 17 and 18] and results obtained, it was proposed to adopt criterion K2 defined as the acceptable maximum amount of SiO<sub>2</sub> grains in a chromite sand sample of  $\leq 1.0\%$ . Consequently, for the number of all analysed grains amounting to 1000, the number of silica sand grains must not exceed 10.

Figures 9 and 10 depict C type grains, i.e. chromite grains bound by means of a binder with high content of Ca and Na. In this case, based on the guidelines in Table 2, analyses of [4] and results obtained, it was proposed to adopt criterion K3 referring to the maximum value of C type grains in a chromite sand sample of  $\leq 0.5\%$ , meaning that if the number of all analysed grains is 1000, the amount of conglomerates containing the binder cannot exceed 5. Moreover, it was found out that unlike the analysis of silica sand grains, the qualitative analysis of the agglomerates formed by the binder and chromite cannot be carried out based on macroscopic observations, but solely on microscopic ones.

If chromite sand fulfils all three criteria, i.e. K1, K2 and K3 simultaneously, its quality is considered perfectly acceptable i.e. final quality is very good. Such a chromite sand type can be used as facing moulding sand base for simple and complex cast steel castings.

However, for chromite sand with the quality considered good, acceptable, it is permissible to meet K1 criterion with reduced Cr concentration, i.e.  $\geq 27$  wt.%, where the acceptable Fe, Al, Mg, Si and O concentration is determined as in K1, K2 criterion is considered met with higher SiO<sub>2</sub> content, i.e.  $\leq 1.5\%$  and K3 criterion with higher C type grains content, i.e.  $\leq 1.0\%$ . Such a chromite sand type can be used as a facing moulding sand base for simple cast steel castings.

In any other case, the failure to meet at least one of the mentioned criteria resulted in deeming the chromite sand quality low, unacceptable which rendered it unusable, for processing reasons, for the base facing moulding sand dedicated to cast steel castings.



Fig. 7. An example of a silica grain marked as type B: a) SEM, mag. 260x, b) EDS spectrograph in spot 1





Fig. 8. Examples of chromite sand impurity with SiO2 grains in macro- (mag. 89x) and microscopic (mag. 240x) view



Fig. 9. An example of a agglomerates of binder – chromite marked as type C: a) SEM, mag. 450x,b) EDS spectrograph in spot 1

Fig. 10. An example of a agglomerates of binder – chromite marked as type C: a) SEM, mag. 350x,b) EDS spectrograph in spot 2





No. of sand		Criterion*				
/ No. of supplier	K1	K2	K3	Final quality	Risk of cast defect occurrence	
1 / 1	OK	NOK	OK	Low and unacceptable	High risk for moulding sand burn-on	
2 / 1	OK	COK	COK	Good	Low risk for pitted skin and moulding sand burn-on	
3 / 1	OK	NOK	OK	Low and unacceptable	High risk for moulding sand burn-on	
4 / 1	OK	OK	OK	Very good	The lack of risk	
5 / 1	OK	OK	OK	Very good	The lack of risk	
6 / 1	OK	COK	OK	Good	Low risk for moulding sand burn-on	
7 / 1	OK	OK	OK	Very good	The lack of risk	
8 / 1	OK	NOK	COK	Low and unacceptable	High risk for moulding sand burn-on	
9 / 1	OK	NOK	NOK	Low and unacceptable	High risk for pitted skin and moulding sand burn-on	
10 /1	OK	OK	OK	Very good	The lack of risk	
1 / 2	OK	NOK	NOK	Low and unacceptable	High risk for pitted skin and moulding sand burn-on	
2 / 2	COK	OK	OK	Good	Very low risk for moulding sand burn-on	
3 / 2	OK	OK	OK	Very good	The lack of risk	
4 / 2	OK	NOK	NOK	Low and unacceptable	High risk for pitted skin and moulding sand burn-on	
5 / 2	OK	OK	COK	Good	High risk for pitted skin	
6 / 2	OK	COK	OK	Good	High risk for moulding sand burn-on	

Table 4. T : . 4 . 6 ....

OK - criterion fulfilled,

COK - criterion fulfilled only for good quality,

NOK - criterion not fulfilled for very good and good quality.

Table 4 presents results for all sixteen chromite sand batches. For five chromite sand batches, very good quality was found, for five it was good, and for the remaining six it was unacceptable. Moreover, the quality of sand from both suppliers was found to be highly similar. For the first supplier, out of ten chromite sand batches, the quality of four was considered unacceptable (i.e. 40%); whereas for the second supplier, out of six chromite sand batches, two were verified negatively (i.e. 33%).

Consequently, it was found out that the grain composition claimed in the chromite sand certificates was true, although the binder content of 0.0% was not. This results from the inability to determine the binder content forming agglomerates with chromite sands of the size similar to that of individual chromite grains using the sieve analysis. What is more, as much as nine out of sixteen chromite sand batches are polluted with silica sand exceeding 0,5% as declared in the certificates. Hence, the differences, as found out during the analyses, between the results and suppliers' certificates, as well as the occurrence of cast steel casting defects, including skin pitting and sand burn-on, require checks of chromite sand quality e.g. by means of the method proposed in this paper.

# 4. Conclusions

Based on the analysis of the test results obtained, the following conclusions were formulated:

The analysed chromite sand batches have varying quality, 1. primarily due to the impure with quartz sand and binder forming agglomerates with chromite grains which are not detectable during sieve analysis.

- The differences, as found out during the analyses, between 2 the results and suppliers' certificates, as well as the occurrence of cast steel casting defects, including skin pitting and sand burn-on, require constant checks of chromite sand quality directly in the foundry e.g. by means of the method proposed in this paper.
- 3 The method of chromite sand quality assessment proposed in this paper, carried out using an optical camera, scanning electron microscopy and EDS analysis is efficient and feasible within 24 hours after sand is delivered to the foundry, provided that the appropriate instruments are in place.
- 4 The validation of the adopted criteria for chromite sand quality assessment revealed that their introduction contributed directly to improved quality of cast steel castings made in Huta Małapanew Sp. z o.o. using moulding sand based on it. Moreover, the data obtained on this basis, once shared with chromite sand suppliers, contributed to improved quality of deliveries to Huta Małapanew Sp. z o.o.

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