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**IMPURE CHROMITE - CAUSE OF
PINHOLE POROSITY**

by

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PHYSICAL METALLURGY DIVISION

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IMPURE CHROMITE - CAUSE OF PINHOLE POROSITY

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SUMMARY OF RESULTS

A sample of chromite submitted for test by Hawker Siddeley (Canada) Ltd., Canadian Steel Foundry Division, Montreal, P. Q., was found to produce pinhole porosity. On pursuing the investigation to discover the cause a new shipment of chromite was obtained. This new sample did not produce pinholes. Carbonates and sulphides were present in the new sample in harmless amounts. Analysis of reclaim sand indicated that these minerals were present in the original chromite sample in much greater amounts. Carbonates and sulphides were probably the cause of the pinhole porosity.

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INTRODUCTION

On May 19, 1965, a request was received from Mr. Willet Tibbits, Manager, Quality Control, Hawker Siddeley (Canada) Ltd., Canadian Steel Foundries Division, for assistance on a pinholing problem they were encountering with their moulding sand. The plant was visited May 20 and 21 to study the difficulty.

The work that had already been done on the problem by Canadian Steel Foundries made them suspect that chromite sand was the source of the trouble. Considerable chromite was being used in cores with very good results, to prevent metal penetration and to promote directional solidification. The chromite then became incorporated into the system, and circulated through the reclamation unit with the silica sand.

On this visit the study of the problem, and a review of the work which had been done by the personnel at the plant, indicated that further investigation could best be done with the facilities of the Mines Branch in Ottawa. A one ton sample of "reclaim" sand was therefore shipped to Ottawa for test.

SEPARATION OF CHROMITE

The sample was tabled to remove the used chromite for further test. The concentrate was rerun in an attempt to make a purer product. The results are shown below:

<u>Product</u>	<u>Weight (lb)</u>	<u>% Cr₂O₃</u>	<u>% Chromite Sand (calculated)</u>
Reclaimed Sand as Received	-	7.75	17.1
Tabled Sand	1835	6.79	15.0
Middlings	64	31.42	69.5
Concentrate	11	25.19	55.5
Chromite Sand	-	45.26	100

Surprisingly, the middlings had a higher concentration of chromite than the concentrate. This is probably because of the presence of other materials such as olivine, zircon, slag, and scale. In further tests, the 11 lb of concentrate was discarded and tests were made with the 64 lb of middlings. In the rest of this report the middlings are designated as concentrate, because they actually contained a higher percentage of chromite.

The results of this test were disappointing from the point of view of plant practice, although the products were suitable for testing the effect of used chromite on casting quality. Therefore, further tests were made to determine the feasibility of making a more chrome-free product. Two methods were tested using the sand as received: tabling to produce a cleaner sand; and the use of a Stearns high intensity magnetic separator. The results were as follows:

	<u>Tabled</u>	<u>Magnetic</u>
Sand, per cent	75.8	72.2
Cr ₂ O ₃ in Sand, per cent	1.37	N.D.
Chromite in Sand, per cent	3.0	N.D.
Concentrate, per cent	24.2	27.8
Cr ₂ O ₃ in Concentrate, per cent	26.67	27.57
Chromite in Concentrate, per cent	59.0	60.8

N. D. - None detected.

These results indicate that the sand could either be tabled or magnetically separated, whichever is cheaper. Humphreys spirals will produce results similar to tabling.

EFFECT OF CHROMITE ON CASTINGS

The two main products of the first tabling operation were mixed in various proportions to determine the effect of used chromite on casting finish.

Test Mixtures

Test mixtures were prepared on a laboratory sand muller to produce green compressive strength and volume similar to the following base mixture:

4500 g Sand
292.5 g Western Bentonite
(sand : clay ratio 100 : 6.5)
45 g Cereal
Moisture to Temper.

The weight of the batches was adjusted to compensate for the greater density of the chromite sand, but the binder additions were kept constant. By assuming that the chromite concentrate was twice as dense as the sand, mixtures with approximately the same green compressive strength were obtained. For example, the formula for the mixture containing 50 per cent chromite was:

3000 g Sand
3000 g Chromite Concentrate
292.5 g Western Bentonite
45 g Cereal
Moisture to Temper.

The properties of the mixtures for the first test series are representative, and are shown in Table 1.

Test Castings

The sand mixtures were used as facing for preparing moulds for the SFSA slab test block. Four heats were poured as follows:

Heat No. 1

- 1 - 100% tabled sand
- 2 - 25% concentrate
- 3 - 50% concentrate
- 4 - 75% concentrate
- 5 - 100% concentrate

Heat No. 2

- 1 - 5% concentrate
- 2 - 10% concentrate
- 3 - 15% concentrate
- 4 - 20% concentrate
- 5 - 25% concentrate - dry sand

Heat No. 3

- 1 - 100% tabled sand
- 2 - 5% concentrate
- 3 - 25% concentrate - roasted sand

Heat No. 4

- 1 - 25% concentrate (28.5% old chromite)
- 2 - 28.5% new chromite

From an examination of the castings it appears:

1. There is a gas-producing reaction when steel is poured into these chromite-sand mixtures. This reaction is worse with increasing amounts of chromite, at least up to the amount in the concentrate, which was 70 per cent. (Figure 1 - 4).

2. The reaction also occurs in dry sand (Figure 2), and in sand which has been burned at 2000°F before the preparation of the mix (Figure 3).

3. There is no significant difference in the behaviour of the new and used chromite (Figure 4).

4. The severity of the reaction is somewhat dependent upon the gas content of the metal (cf 25 per cent concentrate, Figures 1 and 4; and 5 per cent concentrate, Figures 2 and 3).

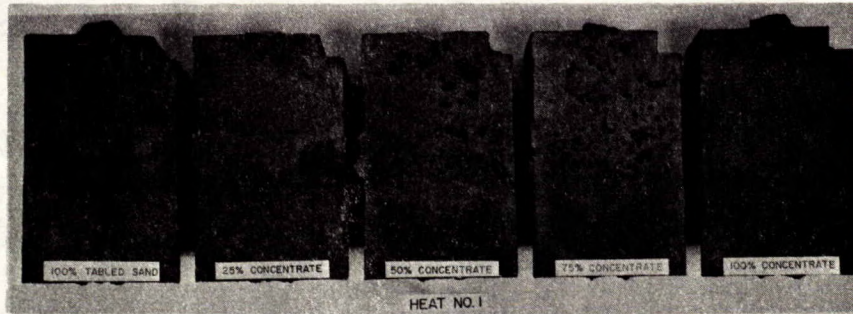


Figure 1. - Castings from Heat No. 1

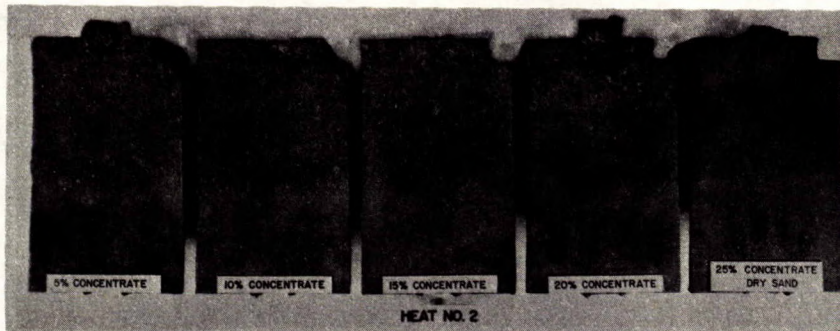


Figure 2. - Castings from Heat No. 2

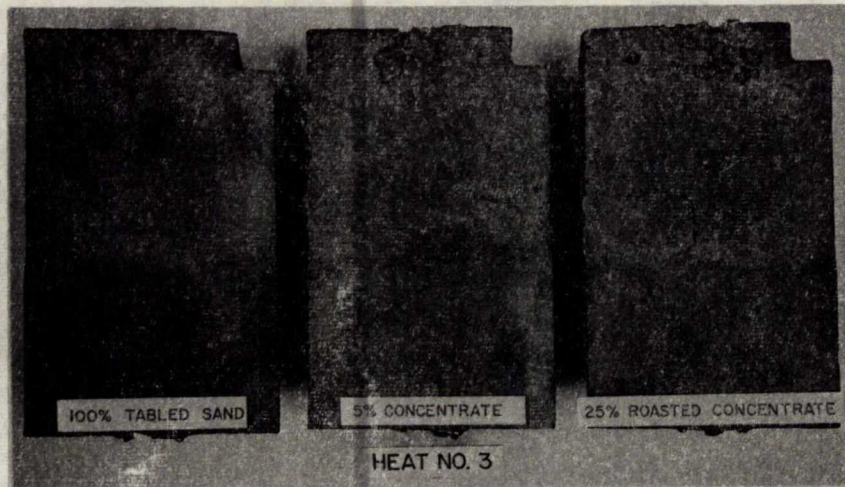


Figure 3. - Castings from Heat No. 3

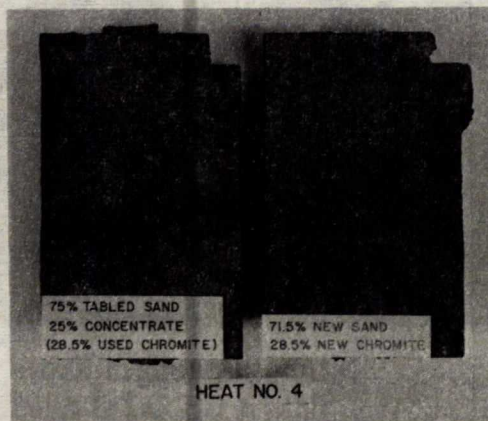


Figure 4. - Castings from Heat No. 4

TESTS ON SECOND CHROMITE SAMPLE

At this point, the original samples of chromite concentrate and new chromite were used up, and another sample of new chromite was obtained for further tests. Surprisingly, the new sample did not produce gas defects such as had occurred with the use of the original material. This suggests that the difficulty was caused, not by the chromite mineral itself, but by some impurity it contained.

The most likely source of extraneous material is the gangue in the original ore. The new sample of chromite should contain the same gangue material, albeit in harmless amounts. Accordingly a close mineral examination was made of the new sample.

Effect of Enstatite

The main mineral impurity of the ore was found to be enstatite. This is a magnesium silicate (MgSiO_3) of the pyroxene family. One of its characteristics is that it often exfoliates on heating; hence it was considered as a possibly harmful mineral. To determine the effect of enstatite on the castings the chromite sand was magnetically concentrated, and tailings and middlings were used in a ratio of 1 part tailings and middlings to 5 parts untreated chromite to prepare an impure chromite sand. This impure chromite, mixed with silica sand in a ratio of 25 parts chromite to 75 parts sand, was used in a mould. The resulting casting did not have gas defects.

From this test it can be concluded that enstatite, the main mineral impurity of the second chromite sample, is harmless in the amounts likely to be found in the marketed material.

Effect of Carbonates and Sulphides

Other impurities present as minor constituents in the second sample of chromite were calcite, magnesite, pyrite, pyrrhotite and coal. The coal, although a gas making material, could not have been an important

factor in this case, because it would not have appeared in the concentrates. As the other minerals are all potential gas producers, the new sample of chromite and the original sample of reclaimed sand were analyzed for sulphur and carbon. The following results were obtained.

	<u>New Chromite</u>	<u>Reclaim Sand</u>
Total C	0.06	0.48
C after solution in HCl	0.025	0.44
Acid soluble C (by difference)	0.035	0.04
Estimated C in original chromite (based on 17% chromite in reclaim sand)		0.24
S	0.004	0.016
Estimated S in original chromite	-	0.1

From these results it appears that the original chromite was much higher in carbonates and sulphides than the new sample. Much of the discrepancy between the total carbon and acid soluble carbon in the new chromite might be attributable to the difficulty of dissolving all of the large size particles of carbonates, associated as they are with chromite. Hence, the estimates of carbonates are likely to be somewhat low.

The above results indicate that the original chromite had 2%-3% carbonates and 0.2% sulphides.

Under the microscope the carbonate was seen to be associated with the chromite. This would explain how it could appear in the concentrates. However, in the tests of reclaim sand heating to 2000° F did not eliminate the source of the trouble, although this should drive the CO₂ off the carbonates and burn any sulphides. In order to determine whether the same heat treatment would render limestone and sulphides harmless two chromite samples were mixed with 2% limestone and 2% sulphides (1% pyrite, 1% pyrrhotite) respectively. These samples were divided and half treated to 2000° F for 1/2 hour, and the other half used without heat treatment in a 50% sand,

50% chromite mixture. The results in Figure 5 show that this heat treatment did not eliminate the pinholes. Probably the hydroxide is as effective as the carbonate as a gas producer; and the unrabbed sulphide could not fully oxidize.

This test shows that the pinholes in the castings made from concentrate could have been caused by carbonates or sulphides.

DISCUSSION

The pinhole trouble experienced with the chromite appears to be an unusual case, caused by some foreign material in the chromite. Unfortunately, this was not realized until the chromite causing the trouble was all used up. Calcite, found in the reclaim sand and in the new shipment of chromite sand, probably is the main cause of the trouble. Pyrite and pyrrhotite, present in the ore in lesser amounts than calcite, would add to the effect.

CONCLUSIONS

1. The pinholes which occurred on the castings resulted from the use of chromite sand.
2. A new shipment of chromite did not cause pinholes. The trouble may be an unusual case caused, not by the chromite mineral itself, but by impurities it contains.
3. Carbonates and sulphides are mineral impurities which cause pinholing. These were found in the new shipment of chromite in harmless amounts. Analyses of the reclaim sand indicates that they were present in the original chromite in much higher amounts.
4. The pinholing was probably caused by carbonates and sulphides, but some other extraneous material may have been partially or mostly responsible.

SUGGESTION

Upper limits for carbon and sulphur content of the chromite ore should be set. Attainable and satisfactory goals appear to be 0.04% acid soluble carbon and 0.005% sulphur.

TABLE 1

Properties of Sand Mixtures for Heat No. 1

Concentrate, %	Moisture, %	Mouldability	Green Compressive Strength, psi	Deformation, in.	Permeability	Dry Compressive Strength, psi
0	3.1	62	9.7	0.0281	212	85
25	2.6	77	9.7	0.0240	151	68
50	2.5	81	8.7	0.0246	146	75
75	2.1	77	10.1	0.0251	91	61
100	2.0	78	8.7	0.0256	77	53