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OTTAWA

MINES BRANCH INVESTIGATION REPORT IR 63-109

**AN X-RAY DIFFRACTION EXAMINATION OF  
FLUE DUST CONTAINING ZINC OXIDE,  
SUBMITTED BY DOMINION FOUNDRIES  
AND STEEL, LIMITED, HAMILTON, ONTARIO,  
IN SEPTEMBER 1963**

by

JOHN F. ROWLAND

MINERAL SCIENCES DIVISION

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AN X-RAY DIFFRACTION EXAMINATION OF FLUE DUST  
CONTAINING ZINC OXIDE, SUBMITTED BY DOMINION  
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SUMMARY OF RESULTS

An X-ray diffraction examination has been made of flue dust that contains zinc oxide in addition to iron oxides. The zinc oxide probably occurs in combination with ferric oxide as a spinel-type compound, zinc ferrite. Examination of screened fractions indicates that this constituent is slightly more abundant in the smaller particles.

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## INTRODUCTION

During October, 1963, samples of flue dust were received for examination by the Physical Chemistry Section of the Mineral Sciences Division, Mines Branch, Ottawa. The flue dust originated with Dominion Foundries and Steel, Limited, Hamilton, Ontario (DOFASCO), and had been deposited in gas scrubbers located in the stack of an oxygen steel furnace. The flue dust was submitted by DOFASCO to the Mineral Processing Division of the Mines Branch, and the problems involved were outlined in correspondence dated September 24, 1963 (see Appendix).

Flue dust is normally agglomerated and charged to the blast furnace, but the material to be examined was stated to contain zinc oxide, which reacts in the furnace and leads to spalling of the refractory wall. An identification of the form in which zinc occurs in the flue dust was requested by DOFASCO. This information would assist in devising a method for removal of zinc-bearing compounds before using the flue dust.

Although it was stated that the flue dust contained zinc oxide, no evidence for the presence of ZnO as a discrete phase has been found either by DOFASCO or in the course of the present investigation at the Mines Branch. Hence, the term "zinc oxide" in this report will be taken to mean ZnO in combination with other oxide(s).

## PREVIOUS WORK ON THE MATERIAL

Investigations done by DOFASCO indicate that the concentration of zinc, calculated as zinc oxide, is generally between 5 and 8%, although it can range from 0 to 15%. No crystalline constituents containing zinc oxide have been detected by X-ray diffraction analysis, although the possible presence of zinc spinel ( $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$ ) may have been masked by the abundant iron spinel, magnetite ( $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ ). Amorphous zinc oxide is unlikely to be present, since leach tests do not lead to an efficient removal of zinc. Although not detected by X-ray diffraction analysis, the more acid-resistant spinel form was thus suspected of being present.

The sample of flue dust was submitted by Mr. D.E. Pickett, Mineral Processing Division, to the Analytical Chemistry Subdivision of Mineral Sciences Division for a chemical analysis (1), the results of which are given below. The analysis confirmed the zinc concentration reported by DOFASCO.

Total Fe	60.08%
Fe <sup>++</sup>	10.33
CaO	3.42
MgO	0.87
Al <sub>2</sub> O <sub>3</sub>	0.13
MnO	1.55
C	0.55
SiO <sub>2</sub>	1.42
ZnO	5.13
H <sub>2</sub> O (+110°C)	1.26

The material received by the Physical Chemistry Section consisted of five sized fractions in addition to the original sample submitted to the Mineral Processing Division, the fractions having been screened from the head sample of the flue dust. The reason for the fractions having been made was not explained, and no details were given of further work being done in the Mineral Processing Division on the sample of flue dust.

#### EXPERIMENTAL PROCEDURE AND RESULTS

The sample of flue dust as submitted by DOFASCO and the five sized fractions were examined individually by X-ray diffraction analysis. A small amount of each material was mixed with collodion, and the mixtures rolled into cylinders of about 0.1 mm diameter and allowed to harden. The solid rolling specimens were mounted in 57.3 mm diameter Debye-Scherrer cameras, and X-ray diffraction patterns were obtained using filtered CoK radiation.

The diffraction patterns were interpreted by comparison with data in the X-ray Powder Data File issued by the American Society for Testing and Materials, or by direct comparison with available standard films. The cubic unit-cell dimensions for the two spinel-type compounds found to be present were calculated from the appropriate diffractions without applying film shrinkage corrections, and must be considered as approximate values only. The broadness of the lines in the back-reflection regions did not justify correcting for shrinkage, since the accuracy would not have been increased.

The following limitations of the X-ray diffraction technique must be noted. Crystalline components that are present in quantity less than about 5% of the total will probably not be detected, and those less than about 2% will almost certainly not be detected. Any amorphous material present cannot be identified, and its presence can only be detected when a substantial amount occurs. In this investigation, the relative abundance of the constituents was assessed solely on the basis of the relative strengths of their diffraction patterns, and must be considered as an approximation.

The constituents identified in the X-ray diffraction patterns are tabulated below. The identified compounds are listed in the same order for all samples, rather than in order of abundance in each sample.

The amounts of spinel #2 and of wüstite present in the samples would not normally have been reported with such apparent precision, but would have been stated as being present as trace or small trace, only. Small variations among the samples were detected in the X-ray diffraction patterns, however, and are indicated by the estimated amounts given in the table. None of the patterns suggested the presence of any appreciable amorphous material, although small amounts may be present; the possible presence of amorphous material was not included in the tabulation.

TABLE 1

Results of X-ray Diffraction Examination

Material Examined		Constituents Identified
Flue dust as submitted by DOFASCO		Major: Spinel #1 ( $a = 8.395 \text{ \AA}$ ), Minor: Hematite ( $\text{Fe}_2\text{O}_3$ ), Trace: Spinel #2 ( $a = 8.43 \text{ \AA}$ ), Very small trace: Wüstite ("FeO").
Sized fractions	+65 mesh	Major: Spinel #1, Small minor to trace: Hematite, Not detected: Spinel #2, Very very small trace: Wüstite.
	+100 mesh	Major: Spinel #1, Small minor: Hematite, Small trace: Spinel #2, Small trace: Wüstite.
	+150 mesh	Major: Spinel #1, Small minor: Hematite, Very small trace: Spinel #2, Very small trace: Wüstite.
	+200 mesh	Major: Spinel #1, Minor: Hematite, Small trace: Spinel #2, Small trace: Wüstite.
	+325 mesh	Major: Spinel #1, Minor: Hematite, Trace: Spinel #2, Very small trace: Wüstite.

## DISCUSSION OF RESULTS

The results of the X-ray diffraction analysis indicate that the flue dust contains a large amount of one spinel-type compound, a lesser amount of ferric oxide (hematite), a small amount of a second spinel-type compound, and a very small amount of ferrous oxide (wüstite). The abundant spinel #1, with unit-cell dimension,  $a = 8.395 \text{ \AA}$ , was used as a reference for estimating the relative amounts of the other constituents in the sized fractions. For hematite there is a definite trend towards increasing abundance in the smaller size fractions. For spinel #2, with  $a = 8.43 \text{ \AA}$ , there is, in general, more present in the smaller size fractions, but the trend is not as definite as for hematite. There is no consistent pattern for the abundance of wüstite in the sized fractions.

It is possible to indicate the chemical composition of the spinel-type compounds by comparing the measured unit-cell dimensions with those reported previously for various spinels (2). The large amount of iron oxides present indicates that the abundant spinel #1 is close to magnetite in composition. Pure artificial  $\text{Fe}_3\text{O}_4$  has a unit-cell dimension,  $a = 8.434 \text{ \AA}$ , but substitution by other divalent or trivalent ions normally takes place in natural occurrences, and apparently always decreases this value. A typical natural magnetite with  $a = 8.396 \text{ \AA}$  has been reported, and this value is close to the average for all reported magnetite unit-cell dimensions. Since this value is almost identical with the measured unit-cell dimension for spinel #1,  $a = 8.395 \text{ \AA}$ , this constituent almost certainly is essentially  $\text{Fe}_3\text{O}_4$ .

Zinc spinel or zinc ferrite ( $\text{ZnFe}_2\text{O}_4$ ) has a unit-cell dimension variously reported as  $8.419 \text{ \AA}$  to  $8.449 \text{ \AA}$ , but not below this range except at elevated temperatures (2). Pure zinc ferrite is not known naturally, all occurrences having appreciable iron (ferrous) substituting for zinc, or manganese substituting for either zinc or iron. The unit-cell dimension of spinel #2 could be measured even less accurately than that of spinel #1 since it was present in only a trace amount. The measured value,  $a = 8.43 \text{ \AA}$ , for spinel #2 is comparable to that for  $\text{ZnFe}_2\text{O}_4$ , however, and this constituent could be zinc ferrite, but this cannot be stated definitely.

Although the unit-cell dimensions of magnetite and zinc ferrite are similar, and both are variable over a range of values, it should be possible to recognize the simultaneous occurrence of these two compounds if they are present as separate phases and not as a single solid solution. Spinel #2 was identified in the X-ray diffraction patterns of this investigation, however, chiefly because such a constituent was suspected as being one form in which the zinc oxide might occur. The diagnostic diffractions, which are

in the back-reflection region of the film, are so faint and broad that this constituent could easily have remained undetected. The diffractions in the front-reflection region are completely masked by the diffractions of the more abundant spinel #1.

The simultaneous existence of two spinel-type compounds, particularly with the same trivalent ion, is rare in natural occurrences (3), but it is not unknown. This phenomenon has been encountered in several investigations in the Mines Branch (4). Generally, complete solid solution occurs, resulting in one spinel-type compound. If two compositions form at different times and do not mix later, however, they are unable to reach equilibrium and two spinel-type compounds could then co-exist. This may have happened during the formation of the flue dust, with the zinc oxide being deposited over a short period of time and unable to diffuse through all the iron oxides.

## CONCLUSIONS

The X-ray diffraction examination confirms that the flue dust consists essentially of iron oxides, principally as magnetite, but with some hematite and a small amount of wüstite. On the basis of somewhat inconclusive X-ray diffraction evidence, the zinc oxide, stated by DOFASCO to be present, is considered probably to occur in combination with ferric oxide as a second spinel phase, zinc ferrite; this constituent appears to be slightly more abundant in the smaller particles.

## REFERENCES

1. F.W. Brethour, Mineral Sciences Division Internal Report MS-AC-63-1268, October 17, 1963.
2. J.D.H. Donnay and W. Nowacki, "Crystal Data", The Geological Society of America Memoir 60 (1954).
3. C. Palache, H. Berman and C. Frondel, "The System of Mineralogy", 7th Edition, Vol. 1 (1944).
4. E.H. Nickel, "The Composition and Microtexture of an Ulvöspinel-Magnetite Intergrowth", Can. Mineralogist, Vol. 6, Part II, 191-199 (1958).



APPENDIX

DOMINION FOUNDRIES AND STEEL, LIMITED

P.O. Box 460

Hamilton, Ontario

24 September 1963

Mr. L.E. Djingheuzian,  
Chief, Mineral Processing Division,  
Mines Branch,  
40 Lydia Street,  
Ottawa, Ontario.

Dear Mr. Djingheuzian:

In reference to the sample of flue dust given to you by Mr. Walsh, it is the dust collected from the oxygen furnace stack gas by our gas scrubbers. Normally, it would be our intention to agglomerate the dust and charge it to the blast furnace. However, it has zinc oxide in it, which gets reduced in the blast furnace; the zinc vaporizes and recondenses on the refractory wall causing the refractory to spall off. Therefore there is a great deal of interest in finding a method to remove the zinc oxide from the iron oxides in the dust.

Our investigation to date indicates that the concentration of zinc oxide in the dust can range from 0 to 15%. Generally, however, it is between 5 and 8%. X-ray analysis has not told us what mineral form the zinc is in. I suspect that it is probably in the spinel  $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$  and consequently the lines are confused with those of the iron spinel  $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ . The zinc could also be an amorphous  $\text{ZnO}$ , but when trying some leach tests, no efficient removal of the zinc was accomplished. This prompted the opinion that the zinc was in the more acid-resistant spinel form.

Thanks very much for your consideration of the problem. If I can be of any more help, or if you need more sample, please do not hesitate to contact me.

Yours very truly,

Noel Thomas,  
Research Metallurgist.

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JFR:DV