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EFFECT OF BARIUM OXIDE VOSCOSITY OF NATURAL E	E AND MANGANOUS OXIDE ON THE BLAST FURNACE SLAGS
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SUPPLEMENTARY HOTES	12. SPONDORING MLITARY ACTIVITY
SUPPLEMENTARY NOTES	Foreign Technology Division Wright-Patterson AFB, Ohio
ABSTRACT	Foreign Technology Division Wright-Patterson AFB, Ohio
A study was made of the the viscosity of natu: Kremikovtsi Metallurg: slags with basicity of cosity with an increas cent, and there are no curves. There is almost MnO, while there is a With an increase in Mi analogy with the data crease in viscosity is while at 15, 20, 25 and pattern of thinning and varying quantities is basicity 0.70. A stri- found with an increase with a decrease in ba	he effect of MnO in a wide range on Wright-Patterson AFB, Ohio Wright-Patterson AFB, Ohio ical Combine with basicity given. In f 1.32 there is an increase in the vis- se in MnO content to 5, 10 and 15 per- o significant differences between given ost no change in viscosity at 20 percent significant decline at 25 and 30 percent nO content with basicity 1.00, a certain for basicity 1.32 is observed. An in- s observed only at 5 and 10 percent MnO, nd 30 percent the MnO shows a strict ction. The thinning effect of MnO in most strongly pronounced at the lowest ict pattern of viscosity also decline sicity from 1.32 to 1.00.

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UNEDITED ROUGH DRAFT TRANSLATION

by Joint Publications Research Services

EFFECT OF BARIUM OXIDE AND MANGANOUS OXIDE ON THE VISCOSITY OF NATURAL BLAST FURNACE SLAGS

By: I. Vulchev

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PREPARED BY:

TRANSLATION DIVISION FOREIGN TECHNOLOGY DIVISION WP-AFB, OHIO.

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Date 12 April 1972

BULGARIA

EFFECT OF BARIUM OXIDE AND MANGANOUS OXIDE ON VISCOSITY OF NATURAL BLAST-FURNACE SLAGS

[Article by Ivan Vulchev, Higher Institute of Chemical Technology: Sofia, Rudodobiv i Metalurgiya, Bulgarian, Vol 22, No 12, 1967, pp 33-32]

Effect of MnO

In the production of cast iron from Kremikovtsi iron ore the slag is characterized by increased BaO and MnO content. In our country (1) a detailed study has been made of the effect of BaO on the viscosity of Kremikovtsi slag. The present study determined the effect of MnO (1.5-30 percent) on the viscosity of natural slag whose chemical composition is given in Table 1.

Up until now publications have devoted comparatively little space to determination of the effect of MnO on the viscosity of blast-furnace slags. S. K. Trekalo (2) made a detailed study of the effect of MnO on the viscosity of blast-furnace slags with basicity $CaO/SiO_2=0.96-1.88$ and 0.16-

23.55 percent MnO. The author established that the addition of 20-23 percent MnO considerably widens the temperature range in which the slags remain fluid enough. This holds true especially for slags with a higher basicity. For these it can be seen that there is a sharp decrease in viscosity with the addition of 2-3 percent MnO, while the thinning action of MnO declines to a certain extent as further additions are made.

M. Ya. Ostroukhov (3) studied the effect of MnO (2.15-11.09) on the viscosity of four groups of blast-furnace slags with a basicity of 0.59-0.94. For the first group with a basicity of 0.93 and 19.62 percent Al_2O_3 , viscosity at 1350° C declines from 21.2 to 13.5 poises with the addition of 8.75 percent MnO. For the second group with a basicity of 0.59, viscosity declines from 72.0 to 24.8 poises with the addition of 9.66 percent MnO, 23.95 poises with 4.28 percent MnO. For the third group of slags with a basicity of 0.82, viscosity declines from 32.0 to 14.5 poises with the addition of 11.09 percent MnO, 19.36 poises with 4.29 percent MnO. For the last group with a basicity of 0.94 and 13.77 percent Al_2O_3, viscosity at

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Key I

Serial number Designation Chemical composition of slags, % Viscosity, poises

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the same temperature declines from 10.8 to 7.8 poises with the addition of 2.15 percent MnO.

According to F. Hartmann (4), there is an almost continuous decline in viscosity with an increase in the MnO content of blast-furnace slags to 25 percent, while after this quantity a certain increase is observed.

I. P. Semik (5) studied the viscosity of blast-furnace slags and established that MnO thins acid slags more than basic slags.

I. D. Balon (6) studied the effect of FeO and MnO cr the viscosity and start of crystallization of early blast-furnace slags. Owing to the insufficient number of experimental data the author draws conclusions which are at variance with most studies in this field. The author believes that with an increase in the quantity of MnO there is a rise in the temperature at which crystallization begins and a slight drop in viscosity.

I. P. Bardin et al. (7) determined the effect of Fe0 and Mn0 on the mineralogical composition and viscosity primarily of synthetic blast-furnace slags. Four groups of slags with a basicity of B=0.80, 1.00, 1.26 and 1.50 were used for the study. A rather significant drop in viscosity occurs with the addition of over 5 percent Nn0. With a further increase in Mn0 (to 20 percent), viscosity changes, though not according to a strict pattern, with a tendency towards a decline.

A. M. Chernyshev (8) studied the effect of Mn() and FeO on early blast-furnace slags.

N. L. Zhilo and L. M. Taylev (9) studied the viscosity of natural early, intermediate and final slags in the production of blast-furnace ferromanganese. The viscosity of the final slags in ferromanganese production is 0.5-3.5 poises at a temperature above 1300° C and the higher ti.: MnO content and the lower the CaO/SiO₂ ratio, the lower the viscosity and the crystallization temperature. The lowest viscosity is found in slag with 15-16 percent MnO and CaO/SiO₂ ratio of no more than 1.3.

Sh. M. Mikashvili et al. (10) studied the viscosity and mineralogical composition of the synthetic ternary system $Mn0-Si0_2-Al_20_3$. The most fluid slags are obtained with an average $Si0_2$ content of 2.0-35 percent. Mn0 50-75 percent and Al_20_3 0-25 percent. The lowest viscosity is obtained with 20 percent Al_20_3 , 55 percent Mn0, 25 percent $Si0_2$ and low temperatures. Of the ternary diagram the most fluid slag at high temperatures has 65 percent Mn0, 30 percent $Si0_2$ and 5 percent Al_20_3 .

A. V. Rudneva et al. (11) studied the viscosity of four-component synthetic slag (K_20 -CaO-Al₂0₃-S10₂) with the addition of 0-40 percent MnO (with Al₂0₃ \approx 5 percent, K_20 -6-18 percent, CaO/S10₂=0.5-1.16). Manganous oxide

- 3 -

reduces the viscosity and crystallization temperature only within certain limits for slags with a basicity of 0.5-0.89 for up to 20 percent MnO and 0.84-1.16 for up to 10 percent MnO.

F. P. Glasser (12) has made one of the most detailed studies of the ternary system $CaO-MnO-SiO_2$, but the article does not go into the question of its viscosity,

It can be sen from this survey of the literature that there are certain contrain tions in the results obtained, which we due to deficiencies in research methods, for example unsuitable viscosimeters, inaccuracies in temperature determination, small number of experimental data, simultaneous fluctuations in the content of several components, etc.

Our studies were performed on natural blast-turnace slag of melts No. 4333 (M 1302), serial No. 22 (Table 1), of which three semisynthetic series are composed. The first samples have the designations M 1302. M 1002 and M 0702 (the letter M signifies that they contain MnO, the first two digits denote basicity multiplied by ten, and the last two digits the percentage content of MnO).

The studies were performed at three different basicities -- $CaO/S10_2$ = 1.32, 1.00 and 0.70, with the MnO content increasing to 30 percent. The addition of 310_2 to the natural slag (No. 4333) with a basicity of 1.32 gave the other two series with basicity of 1.00 and 0.70.

Viscosity was determined by a viscosimeter with damped oscillations of the spindle (13).

Figures 1 and 2 show the effect of MnO on the viscosity of slags with a basicity of $B=CaO/SiO_2=1.32$. It can be seen from Figure 1 that with an

increase in MnO to 5, 10 and 15 percent no appreciable difference occurs in the viscosity of the slag between 1550 and 1450° C. Below this temperature range the slags become more viscous. At 1425° C initial sample No. 22 has 3.7 poises, and derivatives thereof (No. 23, 24 and 25) about 6.5-7 poises, while at 1400° C they have about 4 and 14 poises respectively. The η -t curves for 5, 10 and 15 percent MnO almost converge, from which it follows that the thickening effect is the same for the three different MnO contents and B=CaO/SiO₂=1.32. The addition of 20 percent MnO gives slag whose η -t dependence almost coincides with initial sample No. 22, which has 2 percent MnO. With an increase in MnO to 25 percent, viscosity declines appreciably at all temperatures and the slag becomes longer, having a viscosity of 7.5 poises at 1300° C. The slag with 30 percent MnO is even more fluid and has a viscosity of 4.7 poises at the same temperature.

It can be seen from Figure 2 that at high temperatures $(1550-1500^{\circ} \text{ C})$ the addition of 5-30 percent MnO has almost no effect on the viscosity of the slag with a high basicity (B=1.32). At temperatures below 1425° C the slags

- 4 -

thicken with the addition of 5 percent MnO, and with a further increase in MnO the viscosity remains the same or declines, a second maximum being observed at 20 percent MnO. After this maximum the slags are markedly thinned at 25 and 30 percent MnO and remain quite fluid at a temperature below 1300° C.

Figures 3 and 4 show the effect of MnO on the viscosity of semisynthetic blast-furnace slags with B=1.00. From Figure 3 it can be seen that the slags become more viscous with an increase in MnO to 5 or 10 percent, but sample No. 31 is more fluid than slag No. 29 below 1300° C. An increase in the MnO content to 15 percent does not change the viscosity between 1550 and 1350° C, but belox 1350° C slag No. 32 is more fluid. Viscosity declines at all temperatures with a rise in MnO to 25 percent, and at 1250° C it is only 9 poises. A 30 percent MnO content gives the most fluid slag with the lowest viscosity -- 0.8 poise at 1550° C, and it reaches 4.9 poises at 1250° C. It can be seen from Figure 4 that at high temperatures ($1550-1500^{\circ}$ C) the addition of 5-30 percent MnO has almost no significant effect on viscosity. At temperatures below 1450° C a maximum is obtained with 5 percent MnO, after which viscosity declines with a rise in MnO. It is lowest at 30 percent MnO.

Figures 5 and 6 show the effect of MnO on the viscosity of semisynthetic blast-furnace slags with a bericity of 0.70. It can be seen from Figure 5 that with an increase in MnJ to 5 percent, viacosity declines above 1450° C and rises below this temperature. A very strict pattern of increase in the fluidity of the slag is observed with a further increase in MnO to 30 percent. Its thinning action is observed at all temperatures, being most clearly pronounced at temperatures below 1425° C. Figure 6 shows that the slags become more fluid with an increase in the amount of MnO to 30 percent. A certain increase in viscosity with in increase in MnO to 5 percent is observed only at temperatures between 1400 and 1375° C. At temperatures below 1400° C it can be seen that the thinning action of MnO is more clearly pronounced with an increase in the quantity thereof. The studies at the three different basicities show that viscosity also declines with a decrease in basicity from 1.32 to 1.00 and rises again with a basicity of 0.70. The increase in viscosity in the case of the basic and neutral slags with the addition of 10-15 percent MnO is also due to the rise in the total basicity of the slags. The thinning effect of MnO may be due to a decrease in the size of the silicon-oxygen anions as a result of the dissociation of manganous oxide and the surrender of its oxygen to them. This may explain the stronger thinning effect of MnO in the case of more acid slags where the anionic complexes are larger. MnO lowers the crystallization temperature of the slags as a result of the introduction of a "weak" Mn²⁺ cation. This being the case, the slags become more fluid. The simultaneous action of MnO on the rupture of the silicon-oxygen anions and the lowering of the crystallization temperature of the slags may explain its stronger thinning action at lower temperatures.

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Figure 6. Effect of MnO on viscosity at different temperatures and basicity 0.70.

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Effect of BaO and MnO

World metallurgical practice has not heretofore been impelled by practical reasons to study the simultaneous effect of BaO and MnO on the viscosity and other physicochemical properties of slag systems. This question has arisen for the first time in our country due to the necessity of finding optimal technological conditions for the use of Kremikovtsi ore.

A study was made of the combined effect of BaO and MnO on the viscosity of natural and semisynthetic blast-furnace slags of the Kremikovtsi MK /Metallurgical Combine/.

For this purpose we used slags of melt No. 4333 (of the first blast furnace), No. 1522 and 1526 (of the second blast furnace), to which BaO was added so as to bring it up by steps of two percentage points to 16 percent, and MnO so as to bring it up by steps of two percentage points to 23 percent. Due to a lack of a sufficient quantity of slag in the last sample the added oxides reached 14 and 21 percent.

The slags are designated, for example BM 1421 -- the BM denoting that they contain barium and manganese simultaneously, the first two digits giving the quantity of BaO, the second two digits the quantity of MnO.

In order to study the effect of BaO and MnO in the projected quantity of 14 and 21 percent with three different basicities, the necessary quantity of SiO_2 was added to initial melts No. 4333 and 1522. The compositions of the natural and semisynthetic slags and their basicity are shown in Table 2.

Figure 7 shows viscosity as a function of the temperature of natural slag No. 4333 with basicity 1.32 and of the semisynthetic slags obtained by simultineously increasing the BaO and MnO by steps of two percentage points from 2.03 and 2.30 respectively to 14 and 21 percent. It can be seen from the figure that the semisynthetic slags become more viscous and shorter by increasing the BaO and MnO content. The only exceptions are samples No. 42 and 43 (BM 1017 and Bm 1219), which are more fluid at 1500 and 1475° C. Slag No. 45 (BM 1623) is extraordinarily thick and its viscosity cannot be determined at all at a temperature below 1500° C.

Figure 8 plots the viscosity of natural slag No. 1522 with basicity 0.94 and the semisynthetic slags obtained therefrom by the addition of BaO and MnO. It is observed that there is a slight increase in viscosity with an increase in BaO to 4 and 6 percent and with an MnO content of 11 and 13 percent respectively, but the slags become a bit longer. With a further increase in BaO to 16 percent and MnO to 23 percent (slag No. 55), a drop in viscosity is observed. Samples No. 51, 52 and 53 are marked by lower viscosity at low temperatures ($1225-1175^{\circ}$ C). Slag samples No. 54 and 55 become shorter and have a viscosity of over 52 poises at a temperature of 1225° C. With a decline in basicity to 0.70 and with 14 percent BaO and 21 percent MnO (No. 57) the slags, on the whole, raise their viscosity

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Table 2

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Serial No. Sample No. (The two-letter designation of Samples 39-47, 49-57, 59-64 is "BM.")

Chemical composition of slags, \$
Viscosity, polses

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Key: 1. Viscosity, poises

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Figures 10 and 11. η -t dependence given a constant content of BaO (14 percent) and MnO (21 percent) w 1 a varying basicity of melts No. 4333 and 1522.

Keyt

- 1. Viscosity, poises
- 2. Temperature, ^oC

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Figures 7, 8 and 9. η -t dependence given a simultaneous increase in BaO and MnO of natural blast-furnace slags No. 4333, 1522 and 1526.

Key: 1. Viscosity, poises

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2. Temperature, °C

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about twofold up to 1350° as compared with the initial slags (No. 48), after which the thickening effect is weaker.

Figure 9 plots the viscosity of slags No. 1526 (sample No. 58) with basicity 1.03 and semisynthetic slags with increased BaO and MnO content. With an increase in BaO to 8 percent and MnO to 15 percent, a certain thinning effect is observed (in the case of No. 61 there is a certain thickening at a temperature below 1275° C). With a further increase in the BaO content to 10, 12 and 14 percent and MnO to 17, 19 and 21 percent respectively, an increase in viscosity is observed, which is more clearly pronounced at temperatures below 1400° C. The slags become shorter and their viscosity cannot be determined below 1300° C. Viscosity increases most sharply in the case of slag No. 64 below 1400° C, rising to 46.0 poises at 1350° C.

Figure 10 plots the viscosity of synthetic slags obtained from melt No. 4333 containing 14 percent BaO and 21 percent MnO with a basicity of 1.32, 1.00 and 0.70. It can be seen that slag No. 44 with basicity of 1.32 is the most viscous and shortest, while No. 46 is the most fluid at a temperature above 1300° C (there is a sharp increase in viscosity below this temperature). Slag No. 46 has the most suitable viscosity for the blast furnace. Sample No. 47 with basicity of 0.70 has the character of long slag. It has a viscosity of over 5 poises at all temperatures. At a temperature below 1250° C it is viscous, but its viscosity can still be measured.

Figure 11 plots the ") -t dependence of synthetic slags with the same BaO and MaO content (14 and 21 percent) as in sample No. 1522. A certain increase in viscosity and shortening of the slag is observed with an increase in basicity. Even greater thickening is observed with a decline in basicity to 0.70, and the slag becomes long.

Figures 12, 13 and 14 plot the isotherms for a BaO/MnO ratio of 0.35-0.77 for slags No. 4333, 1522 and 1526. It can be seen that the curves in Figure 12 for slag with a basicity of 1.32 have minimum viscosity for a BaO/MnO ratio of 0.62-0.63, but up to 1400° C the minimum viscosity is about 18 poises.

The isotherms in Figure 13 for slag No. 1522 have a minimum given the same BaO/MnO ratio, but their viscosity at 1400° C is about 3 poises. The isotherms in Figure 14 have a minimum given a BaO/MnO ratio of 05.3, while their viscosity at 1400° C is also about 3 poises. And the three slags display a sharp increase in viscosity after the minimum.

The study of the effect of BaO and MnO on the viscosity of the three different slags indicates that it is quite specific, but the thickening effect is exhibited especially in the basic slags. This may be due to an increase in the basicity of the slag, which is high anyway.

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Conclusion

1. A study was made of the effect of MnO in a wide range (2-30 percent) on the viscosity of natural and semisynthetic slags of the Kremikovtsi Metallurgical Combine with basicity $B=CaU/SiO_2=1.32$, 1.00 and 0.70.

2. In slags with basicity of 1.32 there is an increase in the viscosity with an increase in MnO content to 5, 10 and 15 percent, and there are no significant differences between the n -t curves. There is almost no change in viscosity at 20 percent MnO, while there is a significant decline at 25 and 30 percent.

3. With an increase in MnC content with basicity 1.00, a certain analogy with the data for basicity 1.32 is observed. An increase in viscosity is observed only at 5 and 10 percent MnO, while at 15, 20, 25 and 30 percent the MnO shows a strict pattern of thinning action.

4. The thinning effect of MnO in varying quantities is most strongly pronounced at the lowest basicity 0.70. A strict pattern of viscosity iecrease is found with an increase in MnO content.

5. Viscosity also declines with a decrease in basicity from 1.32 to 1.00, but rises again at basicity 0.70.

6. The simultaneously effect of BaO and MnO on the viscosity of natural slags and semisynthetic blast-furnace slags obtained from the natural slags was studied.

7. Blast-furrace slag with increased basicity (1.32) from melt No. 4333 significantly increases its viscosity below 1500° C with an increase in the BaO and MnO content. Such slags become shorter and thicker.

8. For blast-furnace slag (melt No. 1522 with basicity 0.94) and the semisynthetic slags obtained therefrom, the 7-t curves form a sheaf up to 1325° C. Only slag with 10 percent Ba0 and 17 percent MnO has a higher viscosity up to 1250° C, but at lower temperatures it is no different from the viscosity of the rest of the samples.

9. There is no substantial change in viscosity with an increase in the BaO and MnO content of natural slag No. 1526 with basicity 1.03 to 8 percent BaO and 15 percent MnO. With an increase in BaO to 10, 12 and 14 percent and MnO to 17, 19 and 21 percent respectively, the slags up to 1425° C have the same viscosity as the slags with a lower content of these oxides, but there is a sharp increase in viscosity under this temperature and they become short.

10. Minimum viscosity is obtained according to the composition and basicity of the blast-furnace slags at different BaO and MnO ratios. The slag with basicity 1.32 (No.4333) at 1400° C has a viscosity about 15 to 20

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times higher than the other two slags (1522 and 1526). It is characteristic that at different temperatures minimum viscosity is obtained at the very same BaO and MnO ratio for the individual series.

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