Niğde Ömer Halisdemir Üniversitesi Mühendislik Bilimleri Dergisi
Niğde Ömer Halisdemir University Journal of Engineering Sciences

Araştırma makalesi / Research article

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Usage of boroxide and ulexite ores in ferromanganese production

Boroksit ve üleksit cevherlerinin ferromangan üretiminde kullanımı

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Abstract

This study investigated the possibilities of using low-grade manganese ores in ferromanganese production by smelting process. It is aimed to increase the consumption areas of boron ores. Fluorspar, ulexite, and boroxide were added to manganese ores, and slag fluidity at determined temperatures was examined. Reference samples without flux were used for comparison. The charge materials were melted in graphite crucibles at 1650 °C for 2 hours. The metal/slag phases were separated from each other and their chemical analyses were made. At the end of the experiments, thanks to boron ores, Mn leakage in the slag phase was reduced to a minimum, while 99% Mn was obtained in the metal phase. As a result, it has been determined that the slag fluidity increases more with boron ores (compared to fluorspar), the smelting time decreases, it is possible to use boron ores in ferromanganese production, and their usage areas can be increased.

Keywords: Ferromanganese, Ulexite, B_2O_3, CaF_2, Smelting, Manganese

Öz

Bu çalışmada, düşük tenörlü mangan cevherlerinin ergitme prosesi ile ferromangan üretiminde kullanım olanakları araştırılmıştır. Bor cevherinin tüketim alanlarının arttırılması hedeflenmektedir. Manganez cevherlerine fluorspat, üleksit ve boroksit ilave edilerek cürufun belirlenen sıcaklıklarda akışkanlığı incelenmiştir. Karşılaştırma için flaksız referans numuneleri kullanılmıştır. Şarj malzemeleri kapaklı grafit potalara konularak 1650 °C sabit sıcaklıkta 2 saat ergitilmiştir. Metal/cüruf fazları birbirinden ayrılarak kimyasal analizleri yapıldı. Deneyler sonunda bor cevheri sayesinde cüruf fazında Mn sızıntısı minimuma indirilirken, metal fazında ise %99 Mn elde edilmiştir. Sonuç olarak bor cevherleri ile cüruf akışkanlığının daha fazla arttığı (fluorspat ile karşılaştırıldığında) ve erime süresinin azaldığı, bor cevherlerinin ferromangan üretiminde kullanılmasının mümkün olduğu ve kullanım alanlarının arttırılabileceği tespit edilmiştir.

Anahtar kelimeler: Ferromanganez, Üleksit, B_2O_3, CaF_2, Ergitme, Manganez

1 Introduction

Manganese has an important role in the iron and steel industry. As an alloying element, Manganese ore increases its toughness, strength, machinability, hardenability, and wear resistance when used in iron-containing products and steels [1]. Manganese ore has two significant properties in steelmaking: its ability to combine with sulfur to form MnS (manganese sulfide) and its deoxidation capacity [2]. Enhances machinability by integrating with sulfur to form a soft inclusion (MnS) in the steel, enabling a consistent built-up edge along with a place for the chip to break. In steels, manganese enhances strength, stiffness, hardness, toughness, hardenability, wear resistance as well as forging and rolling qualities [3]. The chemical properties of manganese ore are similar to those of iron ore. It oxidates in a humid environment. As the temperature increases, it shows a combustion reaction with oxygen and air. It can be decomposed from water at high temperatures. It is easily soluble in diluted mineral acids and releases hydrogen gas. It can form compounds by reacting with many elements such as halogens, nonmetals, sulfur, carbon, oxygen, and nitrogen [4]. It can easily form compounds with oxygen, sulfur, and phosphorus in smelting over 1244°C. For this reason, it is used in the removal of oxygen, phosphorus, and sulfur from metals and especially iron. It forms various alloys with iron, silicon, copper, and aluminum. Ferromanganese (78% Mn) and silicomanganese (65-70% Mn) are the most commonly used alloys. Most of the manganese produced in the world (about 90 percent) is used in the steel industry as an alloying material [5]. Forging, durability, toughness, abrasion, rigidity, and hardness properties of steel can be improved by manganese. Manganese can also be used to remove oxygen and sulfur from steel [6]. Fluorite (fluorspar-CaF_2) contains 51.3% Ca and 48.7% F when pure and is used as a fluxing reagent in metallurgy. The development of basic steel production methods has also increased fluorite production. The use of boron minerals instead of fluorite in the iron and steel industry and ferroalloy production is also becoming widespread. A compact structure slag can be obtained by adding boron products to the slag pollinated in the iron and steel industry. In the iron and steel industry, compact structure slag can be obtained by adding boron products to the dusting slag. Using colemanite with fluorite in steelmaking slag prevents slag dusting. In addition, powder slag, which is an environmental problem, can be converted into a compact structure as a recyclable product [7, 8]. Blast furnace slag is formed as a result of metallurgical processes in blast furnaces in iron and steel plants. The charge rate of

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Geliş / Recieved: 25.08.2023 Kabul / Accepted: 21.10.2023 Yayımlanma / Published: 15.01.2024
doi: 10.28948/ngmuh.1349906

the raw material and the smelting processes affect the chemical structure of the slag. The amount of slag varies according to the amount of material charged. Approximately 0.2-0.6 ton of slag can be obtained from 1 ton of melted hot metal. It contains (by weight) 0.5-0.8% FeO, 35-42% CaO, 35-40% SiO_2, 8-9% MgO, 8-15% Al_2O_3, 0.3-1.0% MnO and 0.7-1.5% S. In the production of high-carbon ferromanganese, there is approximately 20% MnO in the slag composition [9]. This ratio is quite high, especially when considering low-grade manganese ores. This situation also increases the cost of ferromanganese production. For this, it is very important to increase the fluidity of the slag and to reduce the slag smelting temperature. Manganese losses are at maximum levels in the smelting processes with fluorspar, and research is carried out for the use of other fluxes instead of fluorspar. Several studies indicate that boron ores can be used as a replacement product for fluorspar in the iron-steel and ferromanganese production [7, 10-12]. Ferroalloys are used in steel production to remove unwanted elements, control graphite formation, and produce other alloys. According to the purposes of use; it is used to provide metal solidification, to give the final composition to the molten steel as desired, and to make the final deoxidation [13]. In research on the role of carbon in ferromanganese alloy, it has been reported that carbon increases the lattice parameter and product strength of γ-Fe-Mn alloys and strongly suppresses the martensitic transformation ($\gamma \rightarrow \varepsilon$) [14-16].

In this study, it was determined that boron ores used instead of fluorspar reduced the manganese leakage in the slag to 1% and increased the manganese in the metal phase to 99%. As a result, it was determined that the fluidity of slag increased more than fluorspar and the smelting time decreased, and it is possible to use boron ores in ferromanganese production.

2 Material and methods

Boron ores used in the experiments were obtained from the Balıkesir Bigadiç region and manganese ore from the Erzincan-Kemaliye region as run-of-mine. The analyzes of the ores and activated carbon were made in the laboratories of Atatürk University East Anatolia High Technology Application and Research Center (DAYTAM) with the ICP-MS device, and the results are given in Table 1. CaF_2 (fluorspar), CaO and Activated carbon were purchased commercially.

CaF_2 (fluorspar) and CaO with a purity of 99% and a size of 45 microns were used in smelting experiments to compare with boron ores. Activated carbon was used in smelting experiments instead of coke powder. The ores were crushed in a jaw crusher, ground in a ball mill, and sieved with a mechanical sieve for grain size classification. Dimensions of crucibles used in smelting experiments; wall thickness=5 mm, height=120 mm, base thickness=5 mm, and Ø=70 mm, conical shaped, and maximum operating temperature is 3000 °C and made of extruded clay unbound graphite material. The crucible covers have a 10 mm diameter hole in the middle for the gas outlet (Figure 1).

Figure 1. Graphite crucibles used in the experiments

Smelting experiments were carried out in an atmosphere-controlled laboratory furnace (ACF 17/12, maximum temperature 1700 °C, continuous use temperature 1650 °C, and internal volume 12 liters). The calcination process was carried out in a muffle furnace with a maximum temperature of 1200 °C. The ores were classified in -325 mesh grain size by sieving process and used in the experiments.

Two different studies were carried out for calcination processes. In order to remove the natural moisture of manganese ores, they were kept in a drying oven at approximately 120 °C for 8 hours. For ulexite ore, TGA analyses were made according to the results obtained, and the calcination process was applied in the muffle furnace at selected temperatures.

Table 1. Chemical analysis results of the ores and activated carbon used in the experiments

Ore	B	Na	Mg	P	K	Ca	Sr	Ba	Si	Al	Mn	Fe
	Concentration (%)											
Ulexite (calcined)	12.95	3.66	1.71	0.003	0.01	4.22	1.04	0.01	0.18	-	-	-
B_2O_3	29.56	0.06	0.03	0	0.01	0.03	0.001	0	0.01	-	-	-
Manganese ore	-	0.03	0.98	0.1	0.034	0.85	-	-	0.1	0.67	36.3	6.2

	sulfur	ash	humidity	Volatile matter	fixed carbon
Activated carbon (weight-%)	0.028	0.84	0.29	3.48	95.36

TGA analysis results are given in Figure 2. According to the TGA results, it was determined that the chemically bound water contained in 1 g of ore was completely removed after 6 hours at a temperature of approximately 400°C. According to these results, the calcination process was applied to ulexite ore and it was used in smelting experiments.

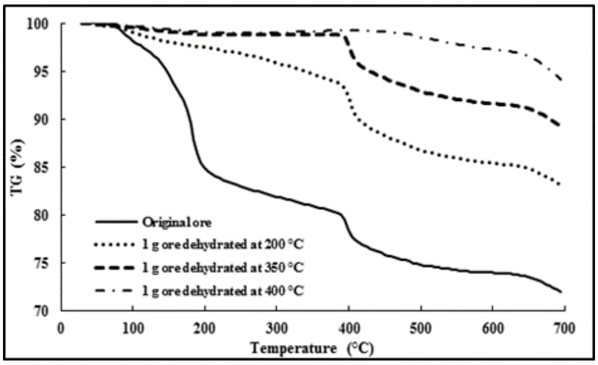

Figure 2. TGA analysis of ulexite ore

The experimental plan of the smelting experiments is given in Table 2. Fluorspar, ulexite, and B_2O_3 added samples, and reference samples without any fluxes were prepared for smelting experiments.

Depending on the fluxes used in the experiments, coding was done according to the basicity ratios, and this coding was used in all experiments. According to the coding;

- **R1**= reference sample with 1% basicity
- **R1.25**= reference sample with 1.25% basicity
- **U1-1**= The charge material consisting of 1 basicity and 2.5% ulexite ore
- **U1-1.25**= The charge material consisting of 1.25 basicity and 2.5% ulexite ore
- **U2-1**= The charge material consisting of 1 basicity and 5% ulexite ore
- **U2-1.25**= The charge material consisting of 1.25 basicity and 5% ulexite ore
- **B1-1**= The charge material consisting of 1 basicity and 2.5% B_2O_3 ore
- **B1-1.25**= The charge material consisting of 1.25 basicity and 2.5% B_2O_3 ore
- **B2-1**= The charge material consisting of 1 basicity and 5% B_2O_3 ore
- **B2-1.25**= The charge material consisting of 1.25 basicity and 5% B_2O_3 ore
- **C1-1**= The charge material consisting of 1 basicity and 2.5% fluorspar
- **C1-1.25**= The charge material consisting of 1.25 basicity and 2.5% fluorspar
- **C2-1**= The charge material consisting of 1 basicity and 5% fluorspar
- **C2-1.25**= The charge material consisting of 1.25 basicity and 5% fluorspar

As an example of how the samples used in smelting experiments are prepared; The mixing ratios for sample **R1** are as follows: for 1 basicity (CaO/SiO_2=1); 100 g manganese ore, 15 g activated carbon (0.15), and 10 g CaO. The mixing ratios for sample **R1-1.25** are as follows: for 1.25 basicity (CaO/SiO_2=1.25); 100 g manganese ore, 15 g activated carbon (0.15), and 15 g CaO. The mixing ratios for sample **U1-1** are as follows: 100 g manganese ore, 15 g activated carbon (0.15), 10 g CaO and 3.125 g (2.5% of the total charge) ulexite for 1 basicity (CaO/SiO_2=1). The mixing ratios for sample **B1-1** are as follows: 100 g manganese ore, 15 g activated carbon (0.15), 10 g CaO and 3.125 g (2.5% of the total charge) B_2O_3 for 1 basicity (CaO/SiO_2=1). The mixing ratios for sample **C1-1** are as follows: 100 g manganese ore, 15 g activated carbon (0.15), 10 g CaO and 3.125 g (2.5% of the total charge) fluorspar for 1 basicity (CaO/SiO_2=1).

Table 2. Compositions of metal and slag obtained at the end of smelting experiments

Sample no		1	2	3	4	5	6	7	8	9	10	11	12	13	14
Activate C/ore		0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Charge basicity (%)		1	1.25	1	1	1	1	1	1	1.25	1.25	1.25	1.25	1.25	1.25
Code		**R1**	**R1.25**	**U1-1**	**U2-1**	**B1-1**	**B2-1**	**C1-1**	**C2-1**	**U1-1.25**	**U2-1.25**	**B1-1.25**	**B2-1.25**	**C1-1.25**	**C2-1.25**
Flax amount(g)	**Ulexite**	0	0	**2.5**	**5**	0	0	0	0	**2.5**	**5**	0	0	0	0
	B_2O_3	0	0	0	0	**2.5**	**5**	0	0	0	0	**2.5**	**5**	0	0
	fluorspar	0	0	0	0	0	0	**2.5**	**5**	0	0	0	0	**2.5**	**5**
Weight (g)	**Metal**	40	41.05	42.19	45.22	45.12	50.87	40.06	43.06	42.75	46.80	45.98	51.75	40.69	43.68
	Slag	37.17	38.42	29.79	21.37	24.84	10.48	33.46	32.63	30.88	22.15	26.01	11.22	34.03	33.13
	Slag / Metal	0.93	0.94	0.71	0.47	0.55	0.21	0.84	0.76	0.72	0.47	0.57	0.22	0.84	0.76
Alloy composition (%)	**Mn**	60.38	65.07	72.35	81.20	73.49	82.17	69.89	78.76	72.7	82.08	75.03	83.36	70.88	79.0
	Fe	13.70	13.54	13.05	12.73	12.89	12.48	13.94	13.37	12.85	12.54	12.70	12.40	13.85	13.02
	Si	0.67	0.60	0.61	0.52	0.57	0.50	02.69	01.70	0.59	0.49	0.51	0.44	2.51	1.62
	C	6.91	6.05	6.79	6.72	6.71	6.54	6.93	6.98	6.70	6.68	6.60	6.27	6.90	6.85
	S	0.010	0.010	0.040	0.060	0.018	0.020	0.003	0.002	0.040	0.060	0.017	0.019	0.003	0.002
	P	0.22	0.22	0.22	0.21	0.21	0.20	0.205	0.20	0.21	0.20	0.20	0.20	0.209	0.202
	B	0.02	0.01	0.29	0.55	0.83	1.85	0	0	0.30	0.55	0.84	1.87	0	0
Slag composition (%)	**CaO**	29.12	34.13	37.48	42.43	38.40	47.89	54.42	52.36	41.72	47.61	43.96	50.43	60.37	58.86
	MnO	15.71	14.17	4.76	1.45	2.76	0.88	23.26	22.66	3.61	1.15	2.03	0.63	21.76	21.97
	SiO_2	37.65	38.25	36.88	36.56	32.27	29.53	58.46	59.70	37.20	37.39	34.07	30.04	60.34	61.5
	Fe_2O_3	0.209	0.216	0.086	0.029	0.133	0.003	0.180	0.20	0.086	0.029	0.127	0.003	0.185	0.229
	Al_2O_3	3.09	2.91	3.51	3.95	3.87	4.43	10.60	10.28	3.04	3.82	3.78	4.10	10.58	10.22
	MgO	4.15	3.92	4.07	5.27	4.62	5.72	5.47	5.02	4.58	5.02	4.28	5.35	5.20	4.98
	B_2O_3	0.31	0.25	2.01	4.09	5.54	9.99	0	0	1.94	4.84	5.51	9.86	0	0

These prepared charge materials were placed in the high-temperature furnace in graphite crucibles and the experiment began. The experiments were carried out in accordance with the experimental plan by smelting it at 1650 °C for 2 hours. After the furnace cooled down, the crucibles were broken. The slag and metal phases were sensitively separated from each other, weighed on a precision scale, and analyzed with ICP-MS. Using the data obtained as a result of ICP-MS, the amounts of B_2O_3, and the other compositions were calculated with the stoichiometric. Table 2 was created with the concentration values found.

3 Results and discussions

3.1 *Effect of bacisity*

In this study, the charge basicity was defined as the ratio of the total weight of CaO to the total weight of SiO_2 in the charge. Slag basicity was adjusted by adding CaO (%99.99 purity) to the charge.

The reduction of the primary oxides from the slag by carbon is shown in Equations 1 and 2 reactions [16]:

$$\mathrm{MnO + C(s) = Mn + CO(g)} \tag{1}$$

$$\mathrm{SiO_2 + 2C(s) = Si + 2CO(g)} \tag{2}$$

Change in the slag basicity affects the activity coefficients of the oxides. The increase in slag basicity increases the activity coefficient of MnO in the slag phase and decreases that of SiO_2. Thus, while it becomes easier for MnO to be reduced to the metal phase, it becomes difficult to reduce SiO_2 (Equations 1 and 2). This situation also coincides with the experimental results [16].

In the slag phase, the MnO concentrations of samples with a basicity of 1.25 are lower than the MnO concentrations of samples with a basicity of 1.00 (Figure 3c). When the **R**, **C**, **U**, and **B** samples in the slag phase are compared, the sample with the lowest MnO concentration is **B2-1.25**. The lowest MnO concentrations were obtained in samples **B** and **C**. While the highest MnO concentrations were obtained in **R** samples, MnO concentrations in **C** samples were lower than **R**'s and higher than in **U** and **B** samples. The SiO_2 concentrations of samples with a basicity of 1.25 in the slag phase are higher than the samples with a basicity of 1.00 (Figure 3d). However, when the **R**, **C**, **U**, and **B** samples in the slag phase are compared, the sample with the highest SiO_2 concentration is **C2-1.25**. SiO_2 concentrations determined in **R** samples are higher than **B** and **U** samples, and lower than **C** samples [16, 17]. In terms of the effect of basicity on the slag phase, the best results were obtained in the experiments using B_2O_3 ores with 1 and 1.25 basicity and 5 g flux addition.

In the metal phase, the Mn concentrations of samples with a basicity of 1.25 are higher than those of samples with a basicity of 1.00. When **R**, **C**, **U** and **B** samples in the metal phase are compared, the sample with the highest Mn concentration is **B2-1.25** (Figure 3a). The lowest Mn concentrations were obtained in **R** samples, while **C** samples were higher than **R** samples but lower than **U** samples. The Si concentrations of the samples with a basicity of 1.25 in the metal phase are lower than the samples with a basicity of 1.00 (Figure 3b).

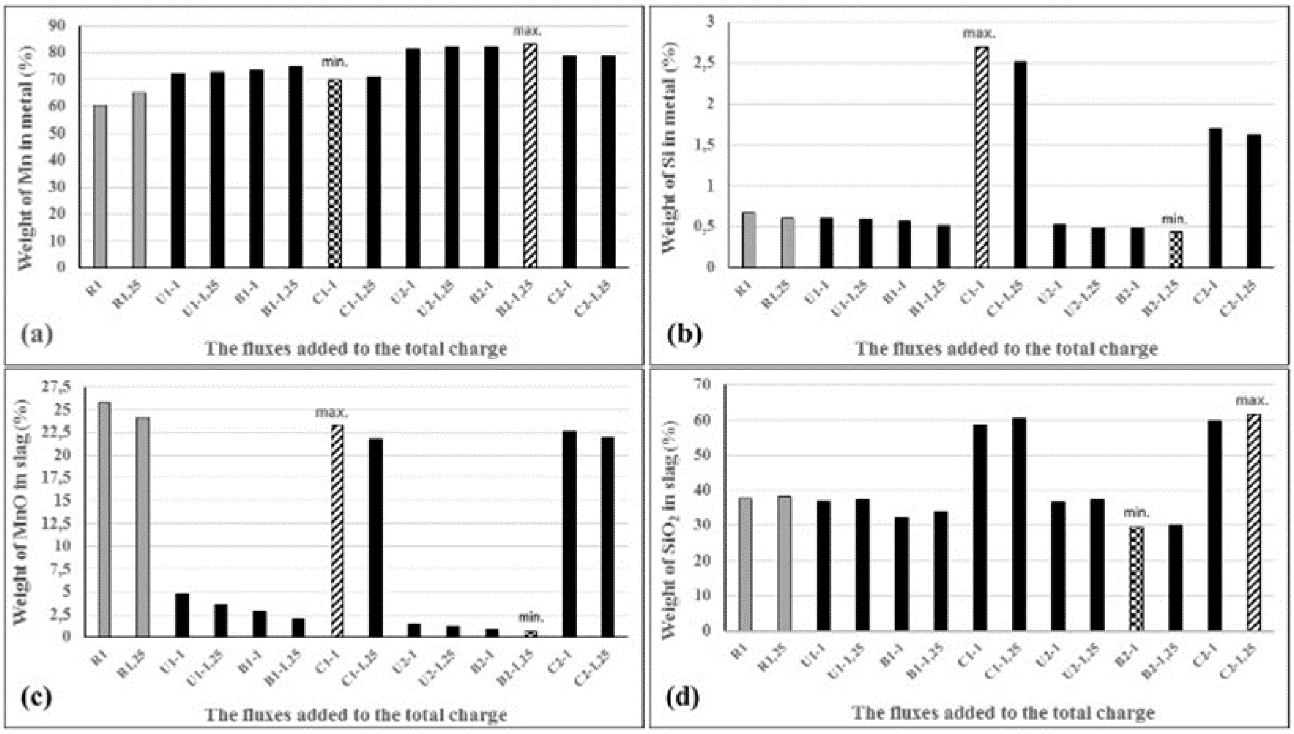

Figure 3. The amounts of Mn (a) and Si (b) obtained in the metal phase, and the amount of MnO (c) and SiO_2 (d) obtained in the slag phase at the end of the smelting experiments

However, when the **R**, **C**, **U**, and **B** samples in the metal phase are compared, the sample with the highest Si concentration is **C1-1**, and it is approximately 3 times higher than the other samples. Si concentrations determined in **R** samples are higher than **B** and **U** samples, and lower than **C** samples. In terms of the effect of basicity on the metal phase, the best results were obtained in experiments using boron ores with 1.25 basicity and 5 g flux addition.

The amount of CaO at 1.25 basicity was determined at higher rates than at 1.00 basicity. (Figure 4a). Adding CaO to the charge to adjust the basicity caused the CaO amounts to be high. The highest CaO amounts were detected in samples **C1-1.25** and **C2-1.25**. It was determined that the amounts of CaO and Si were much less in the samples where boron ore was added instead of fluorspar (Figure 3b, Figure 4a). In studies on the smelting of manganese ore, it has been reported that with the addition of CaF_2 to the system, silicon reacts with CaF_2, and the silicon content in the metal decreases, which is due to the increase in the amount of CaO in the slag (Equation 3) [16,17].

$$SiO_2 + 2CaF_2 = SiF_4(g) + 2CaO \qquad (3)$$

As a result, it was determined that as the basicity increased, Mn, CaO, and Si ratios in boron-added samples were at better values than in fluorspar-added samples (both in the metal phase and the slag phase). It was determined that basicity did not have a significant effect on the amounts of Fe, C, S, P, and B in the metal phase, and the concentrations were below 1% in all samples.

3.2 *Effect of Fluorspar addition*

Fluorspar, which is used to produce steel in blast furnaces, iron, and electric furnaces, decreases the smelting temperature of the slag, increases its fluidity, and facilitates the mixing of sulfur and phosphorus in the iron into the slag. It also increases the smelting rate of the lime in the slag. Thanks to the addition of fluorspar, the metal-slag separation in the system improves due to the increase in slag fluidity [1, 12, 16]. In the smelting experiments using fluorspar, the best results for slag-metal separation were obtained in the sample **C2-1.25** (1.25 basicity and 5 g fluorspar added) compared to the **R1 and R1.25** samples.

Effect of fluorspar on Mn and MnO changes in metal and slag phases: Mn concentrations increased in all samples in the metal phase. Compared to **R** samples, Mn concentrations were higher in **C** samples.

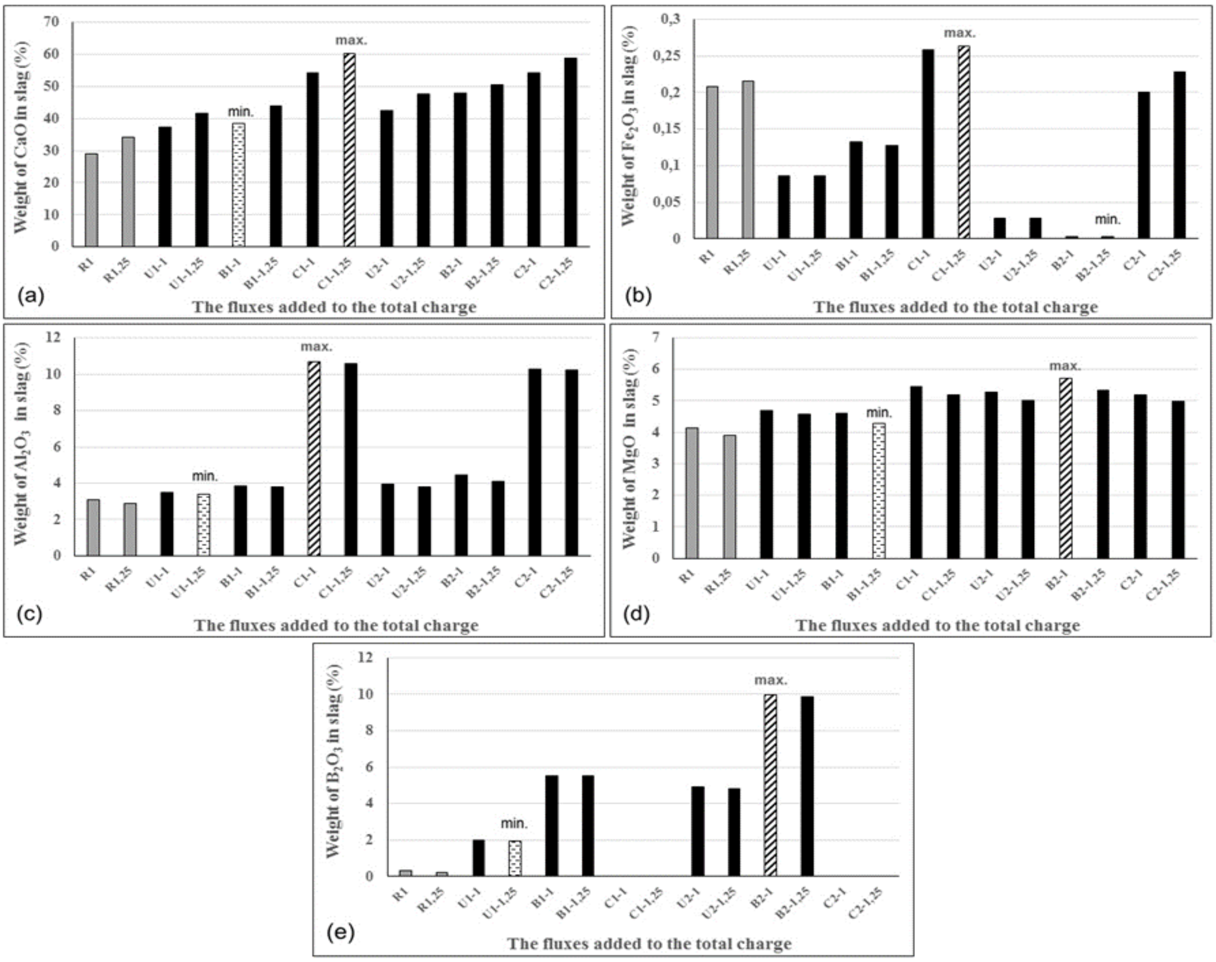

Figure 4. The amounts of CaO (a), Fe_2O_3 (b), Al_2O_3 (c), MgO (d), and B_2O_3 (e) obtained in the slag phase at the end of the smelting experiments

The highest Mn concentration increase rate was determined in the **C2-1.25** sample, with approximately 30%. Here, it can be seen that fluorspar is more effective at the melting temperature compared to **R** samples [1, 16, 17, 19]. In the slag phase, MnO concentrations are slightly lower in **C** samples compared to **R** samples. The highest MnO concentration was determined in sample **C1-1**. Compared to the MnO concentration values of **B** and **U** samples, it is seen that adding fluorspar does not have much effect on preventing MnO leakage in the slag phase (Table 2, Figure 3a, Figure 3c).

Effect of fluorspar on Si and SiO_2 changes in metal and slag phases: Si and SiO_2 concentrations in the metal and slag phases increased in **C** samples compared to **R** samples. The highest Si concentration in the metal phase was detected in the **C1-1** sample, and the highest SiO_2 concentration in the slag phase was detected in the **C2-1.25** sample. Approximately 4-5 times more Si concentration was measured in **C** samples in the metal phase. In the slag phase, this increase is approximately 60%. Considering the **B** and **U** samples, it is seen that fluorspar does not have much effect, especially in preventing more than desired Si transition to the metal phase (Table 2, Figures 3b and 3d) [16-18, 20-22].

Effect of fluorspar on Fe and Fe_2O_3 changes in metal and slag phases: The highest Fe concentration in the metal phase was obtained in the **C1-1** sample. The highest Fe_2O_3 concentration in the slag phase was obtained in the **C1-1.25** sample (Table 2, Figure 5a, Figure 4a, 4b). Fe concentrations in the metal phase are close values in all samples. It is known that in the production of high-carbon ferromanganese, almost all of the iron oxides in the ore are reduced [1, 12, 16, 18]. The fact that Fe_2O_3 in the slag phase is higher in **C** samples (especially compared to **B** samples) can be explained by the fact that the fluidity of the slag increases thanks to boron ores, and the reduction becomes easier.

Effect of fluorspar on C, S and P changes in metal and slag phases: The highest S concentration in the metal phase was obtained in the **U2-1.25** sample, and the P concentration was obtained in the **U1-1** sample. The lowest concentration values were detected in the **C2-1.25** sample. P concentrations were around 0.2% in all experiments. When the S concentrations were examined, the amount of **S** concentration obtained in the **C** samples was 0.01%, while it was 0.06% in the **U2-1.25** sample, where the maximum concentration was obtained. According to these results, it can be said that the effect of **C**, **B**, and **U** samples on S and P reduction in ferromanganese production is negligible (Figure 5c, 5d). When the carbon values in the metal phase were examined, the highest carbon concentration was obtained in the **C2-1** sample, while the lowest carbon concentration was obtained in the **B2-1.25** sample. These results are similar to the concentration values of S and P, and the same comments can be made (Figure 5b).

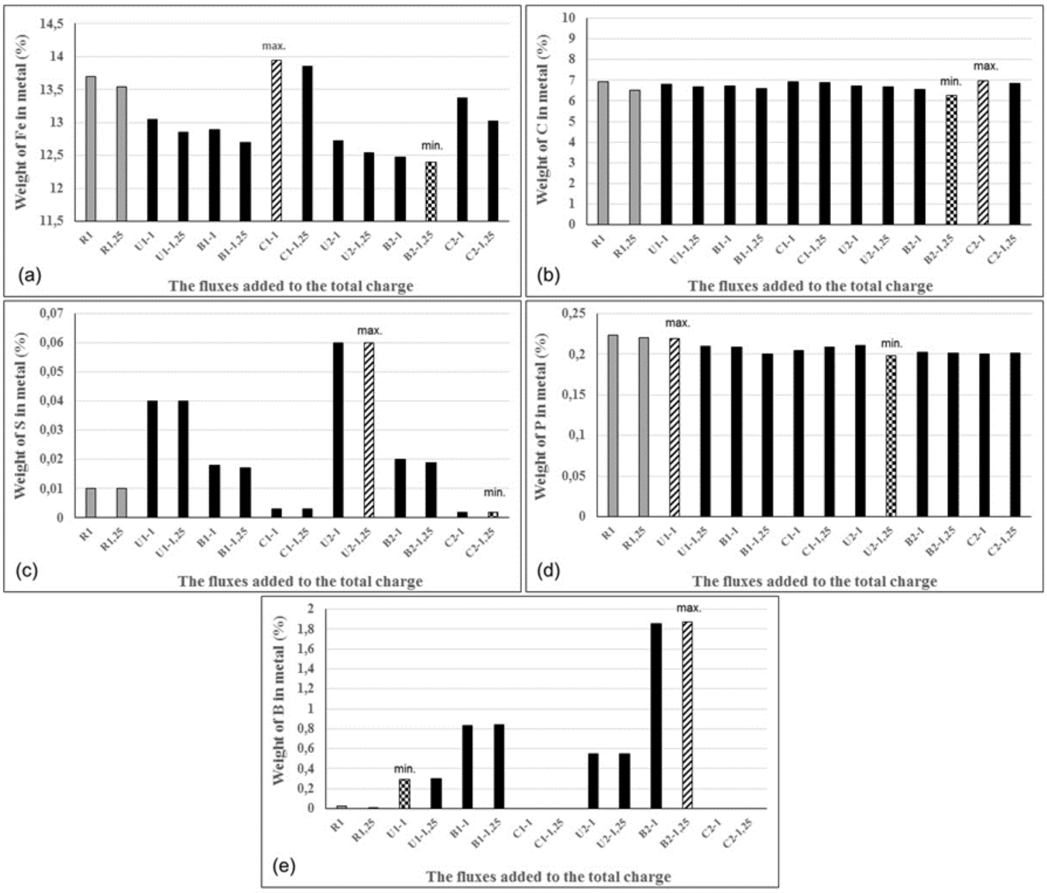

Figure 5. Fe (a), C (b), S (c), P (d), and B (e) amounts obtained in the metal phase at the end of smelting experiments

3.3 Effect of B_2O_3 addition

B_2O_3 flux, which was used to compare with reference samples and fluorspar flux in smelting experiments, gave much better results in Mn, Fe, and Si concentrations in metal and slag phases.

Effect of B_2O_3 on Mn and MnO changes in metal and slag phases: With the addition of B_2O_3, the Mn concentration in the metal phase in all **B** samples increased compared to **R** and **C** samples. The highest Mn concentration in the metal phase is 83.36% in **B2-1.25**. The lowest Mn concentration in the metal phase was obtained in sample **C1-1** with 70.88%. MnO concentrations in the slag phase are higher in **C** samples than in **B** samples. While the highest MnO concentration is 22% in the **C1-1** sample, MnO concentrations are below 3% in **B** samples (Figure 3a, Figure 3c). As a result, it was observed that the B_2O_3 flux added to the charge significantly increased Mn recovery and reduced MnO concentration (compared to fluorspar) [22].

Effect of B_2O_3 on Si and SiO_2 changes in metal and slag phases: The concentration of Si and SiO_2 in the metal phase decreased in all **B** samples compared to **R** and **C** samples with the addition of B_2O_3. While the maximum Si concentration in the metal phase was obtained in the **C1-1** sample, the minimum Si concentration was obtained in the **B2-1.25** sample. While the maximum SiO_2 concentration in the slag phase was obtained in the **C2-1.25** sample, the minimum SiO_2 concentration was obtained in the **B2-1** sample (Table 2, Figures 3b and 3d). As Mn concentrations in the metal increase, Si concentrations decrease. Likewise, the higher the MnO concentration in the slag phase, the greater the Si transition to the metal phase. Boron ores also increase Mn concentrations in the metal phase and thus decrease Si concentrations [1, 12, 16, 22].

Effect of B_2O_3 on Fe and Fe_2O_3 changes in metal and slag phases: Compared to **R** and **C** samples, Fe and Fe_2O_3 concentrations decreased in all **B** samples (Figure 4b, Figure 5a). The lowest Fe concentration in the metal phase and the lowest Fe_2O_3 concentration in the slag phase were obtained in the **B2-1.25** sample. The fact that the amount of iron oxide in the slag phase is higher than in **B** and **U** samples shows that boron ores are more effective in iron reduction [22].

Effect of B_2O_3 on C, S, and P changes in metal and slag phases: When compared with **R** and **C** samples, no significant changes were observed in the amounts of C, S, and P in the B_2O_3 added samples (Figure 5b, 5c, 5d).

Effect of B_2O_3 on B and B_2O_3 changes in metal and slag phases*:* While the highest boron concentration in the metal phase was detected in the **B2-1.25** sample, the lowest B_2O_3 concentration in the slag phase was detected in the **B2-1** sample (Figure 5e, Figure 4e). To obtain ferromanganese it is preferred that the amount of B_2O_3 be high in the slag phase and low in the metal phase.

3.4 Effect of Ulexite addition

Much better results were obtained in Mn, Fe, and Si concentrations in metal and slag phases with ulexite flux, which was used for comparison with reference samples and fluorspar flux in smelting experiments. When compared with B_2O_3, B_2O_3 flux was observed to be better than ulexite.

Effect of ulexite on Mn and MnO changes in metal and slag phases: With the addition of ulexite, the concentration of Mn in the metal phase in all **U** samples increased compared to R and C samples. The highest Mn concentration in the metal phase is in **U2-1.25** with 82.08%. The lowest Mn concentration in the metal phase was obtained in sample **C1-1** with 70.88%. MnO concentrations in the slag phase are higher in **C** samples than in **U** samples. While the highest MnO concentration is 22% in the **C1-1** sample, MnO concentrations are below 5% in the **U** samples (Figure 3a, Figure 3c). As a result, it was observed that ulexite flux added to the charge significantly increased Mn recovery and reduced MnO concentration (compared to fluorspar).

Effect of ulexite on Si and SiO_2 changes in metal and slag phases: The concentration of Si and SiO_2 in the metal phase decreased in all **U** samples compared to **R** and **C** samples with the addition of ulexite. While the maximum Si concentration in the metal phase was obtained in the **C1-1** sample, the minimum Si concentration was obtained in the **U2-1.25** sample. While the maximum SiO_2 concentration in the slag phase was obtained in the **C2-1.25** sample, the minimum SiO_2 concentration was obtained in the **U2-1** sample (Figures 3b and 3d). The results obtained in Mn and MnO concentrations in experiments conducted with ulexite ore are similar to those obtained with B_2O_3 [16, 22].

Effect of ulexite on Fe and Fe_2O_3 changes in metal and slag phases: Fe and Fe_2O_3 concentrations decreased in all **U** samples compared to **R** and **C** samples (Figure 4b, Figure 5a). The lowest Fe concentration in the metal phase and the lowest Fe_2O_3 concentration in the slag phase were obtained in the **U2-1.25** sample. In parallel with the results obtained in **B** samples, the amount of iron oxide in the slag phase in **U** samples is low, indicating that ulexite is also effective in iron reduction [22].

Effect of ulexite on C, S, and P changes in metal and slag phases: When compared with **R1**, **R1.25**, and **C** samples, no significant changes were observed in the amounts of C, S, and P in the ulexite added samples (Figure 5b, 5c, 5d).

Effect of ulexite on B and B_2O_3 changes in metal and slag phases*:* While the highest boron concentration in the metal phase was detected in the **U2-1** sample, the lowest B_2O_3 concentration in the slag phase was detected in the **U1-1.25** sample (Figure 5e, Figure 4e). To obtain ferromanganese it is preferred that the amount of B_2O_3 be high in the slag phase and low in the metal phase.

4 Conclusions

In this study, the possibility of using ulexite and B_2O_3 instead of CaF_2 (fluorspar), which is used as a flux in the production of high-carbon ferromanganese, was investigated and the following results were found;

The increase in slag basicity increased the MnO activity coefficient and decreased the SiO_2 activity coefficient in the slag phase. As a result, MnO was reduced, and the transition of Mn to the metal phase became easier. Likewise, SiO_2 was also reduced, and the transition of Si to the metal phase became difficult (Figure 3, Figure 6) [16, 17, 20, 22]. Thus, by increasing the basicity of the slag, the transition of Si to the metal phase (more than desired) was prevented. In experiments using CaF_2 as flux, it was observed that the concentrations of Si and SiO_2 in the metal and slag phases were higher than in the reference samples. However, in experiments where ulexite and B_2O_3 were used as flux, it was observed that Si and SiO_2 concentrations were lower in the metal and slag phases compared to the **R** and **C** samples (Figures 3b and 3d) [16-19]. As a result, as basicity increases, the Mn ratio increases, the Si ratio decreases, and the ratio of Si in the metal phase to the amount of Si in the charge decreases [1, 12, 16].

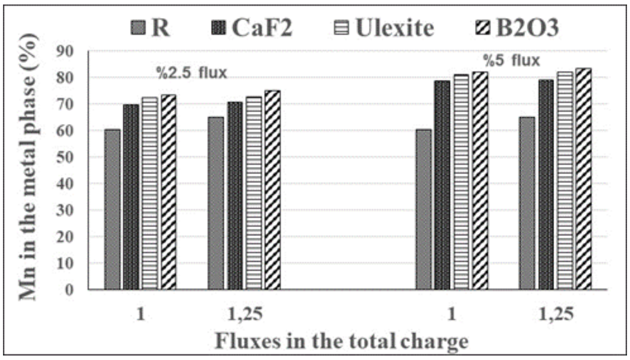

Figure 6. Changes in the concentration of Mn obtained in the metal phase at the end of the smelting experiments

When the fluxes used in smelting experiments are compared;

MnO concentrations in the slag phase are higher in **C** samples (compared to **R** samples). The amount of MnO is approximately 9-10 times less in **B** and **U** samples compared to **C** and **R** samples. The most successful result in terms of MnO yields in the slag phase was obtained in the **B2-1.25** sample (Figure 7). Thus, thanks to boron ores (compared to CaF_2), MnO leakage in the slag phase was reduced to minimum levels, and almost all of the Mn was transferred to the metal phase.

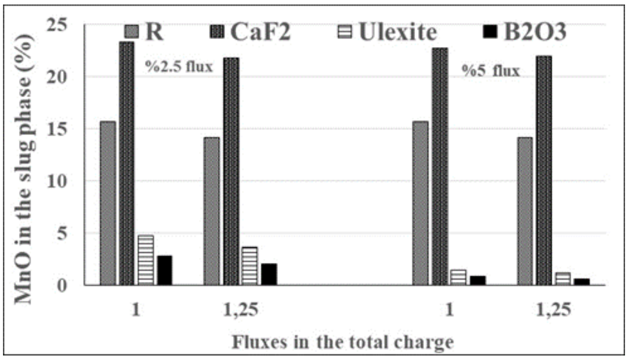

Figure 7. Changes in the concentration of MnO obtained in the slug phase at the end of the smelting experiments

When Fe and Fe_2O_3 concentrations are examined, similar values were obtained in all samples in the metal and slag phases (Figure 8). The minimum Fe_2O_3 concentration in the slag phase was obtained in the **B2-1.25** sample, and the maximum Fe concentration was obtained in the **C1-1.25** sample. The Fe_2O_3 concentration obtained in the **B2-1.25** sample in the slag phase is 0.003% (Figure 4b). These values are close to the iron oxide concentrations reported in the literature in the slag phase in ferromanganese production [1, 12, 16, 18, 22].

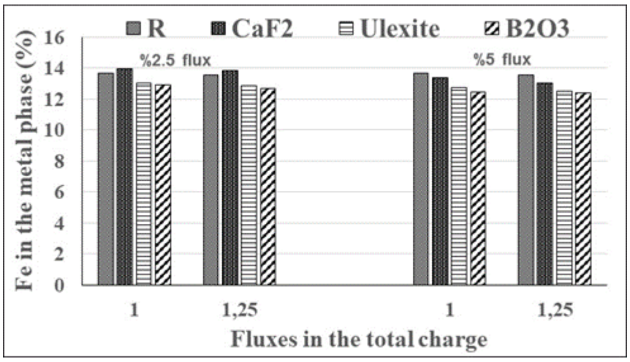

Figure 8. Changes in the concentration of Fe obtained in the metal phase at the end of the smelting experiments

Mn concentrations detected in the metal phase are significantly higher in **B** samples compared to **R** and **C** samples. The highest Mn yield in the metal phase was obtained in the **B2-1.25** sample. Mn yield is approximately 5% higher in **B** samples and 3% higher in **U** samples than in **C** samples. When Figure 6 is examined, the Mn yield is much higher in **B** and **U** samples than in **C** and **R** samples. Using boron ores in ferromanganese production, Mn recovery in the metal phase was more successful than fluorspar. It was determined that the slag/metal ratio was around 0.22 in samples **B** and **U**, while this ratio was 0.7-0.8 in samples **C** (Figure 9).

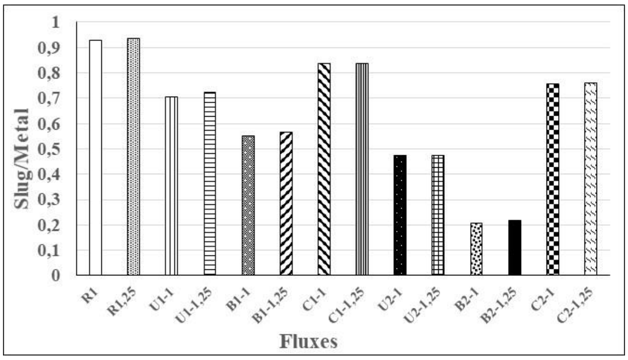

Figure 9. The yield of metal and slag phases at the end of smelting experiments

Research indicating that boron ores provide better slag fluidity than fluorspar, increase the fluidity of the slag and almost completely prevent manganese from mixing into the slag, also supports these results. Additives of B_2O_3 can be successfully used to form high-magnesium liquid steel-making slags. It is shown that 0.37–0.55 % B_2O_3 effectively stabilizes the highly basic slags of the steel and ferroalloy industries [1, 12, 16, 21].

The C concentrations in the metal phases are close to each other in all experiments, and the difference in C content between the samples is around 1%. At the end of the experiments, a high-carbon ferromanganese product was obtained (Figure 5b) [1].

When all experiments were examined, B_2O_3 flux, 1.25 basicity, and 5 g flux amount were determined as the best experimental parameters.

In this study, smelting experiments were carried out with Erzincan-Kemaliye manganese ores, and it was proven that ferromanganese with more than 80% Mn content and high carbon in the metal phase could be produced by using B_2O_3 and ulexite instead of CaF_2 as flux. It has been determined that thanks to the use of boron ores as flux, Mn leakage in the slag phase is minimized, while maximum Mn concentrations can be reached in the metal phase. It has been demonstrated that low-grade Turkish manganese ores can be used in ferromanganese production by minimizing manganese leakage in the slag phase. In addition, it is estimated that energy savings can be achieved in ferromanganese production by producing ferromanganese at lower temperatures since boron ores reduce the melting temperature of slag.

Acknowledgment

This work was supported by Research Fund of the Ataturk University. [Project Number: FYL-2020-8584]

Conflict of interest

The author declares that there is no conflict of interest.

Similarity rate (iThenticate): %12

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