

POTLINING FLUX IN MAKING STEEL

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A study is described wherein spent potlining (from the aluminum industry) is tested as a flux in making alloy steel in an electric arc furnace. Two briquetted variants of said potlining are examined: KARBRIK containing ~30% C = carbon and ~12% F = fluoride, and KALBRIK containing ~4% C and 19% F, respectively. These products are compared with a commercial high grade "SPAR" material containing virtually no C and ~45% F.

The tests are carried out using lime as the basic slag former and with the fluxes added separately to provide approximately the same (initial) amount of F. Clearly, many components are essential to the quality of tapped metal --- but, in this study, S = sulphur content is particularly important.

In terms of general performance, all heats are within specification. Slags produced using KARBRIK and KALBRIK appear more fluid than that obtained using SPAR. By modifying furnace practice, it is shown that KARBRIK can replace not only the SPAR but also the low-S carbon usually added in the furnace charge. Particulate emissions leaving the furnace when using potlining evidence increased amounts of Na and F (over SPAR) --- but these losses are relatively small. The compositions of the slags are similar and show good utilization of Na and F values.

Introduction

An electrolytic pot in an alumina reduction plant is initially lined with insulation (Al_2O_3 , for example) and carbon. In use for different times and under different operating conditions, this lining becomes impregnated with molten electrolyte (mainly Na_3AlF_6). Spent potlining, obtained at the end of the pot's life, therefore, contains variable amounts of C, Na, Al, and F. Analyses of spent potlining have been published, industry-wide, and average values for these quoted elements are 33, 14, 15 and 16 wt%, respectively (1).

There are several routes for disposing of, or recovering values from, spent potlining (1). Among these, in July 1981, the U.S. Bureau of Mines (USBM) published a report (2) outlining the possibility of using spent potlining as a substitute for fluorspar while making iron in a cupola. The results of this investigation, sponsored by Alcoa, were encouraging.

The purpose of the present study was to examine this possibility further --- using briquetted products made from spent potlining. Kaiser Aluminum and Chemical Corp. (KACC) teamed up with Columbia Steel Casting Co. (CSCC) to test this approach, making a number of test heats during the six-month period: February through July, 1982.

More recently, the USBM published a second report (3) --- extending the use of potlining to making steel in a basic oxygen furnace (BOF).

Test HeatsCSCC Furnace

CSCC makes alloy steel castings for various end uses. In conducting our tests, we aimed to disturb the everyday operation of the CSCC foundry as little as possible. The tests were, therefore, carried out using a (nominal) 4-ton Whiting Corp. electric arc furnace making standard production heats on a 2 shift/day basis. Said tests were conducted periodically through the aforementioned six-month period --- first making KARBRIK, followed later by KALBRIK heats. These tests were interspersed with regular SPAR runs.

In general, each charge to the furnace took ~1 hr to melt (~2 hr if the furnace was initially cold) and a further ~3/4 hr until the steel was tapped into the ladle. Occasionally, additional time was spent in extending the electrodes or waiting on the casting shop, etc.

The condition of the 4-ton furnace is routinely checked. The magnesia-based refractory receives particular attention and is patched perhaps as frequently as every 24 or 48 hr. Because of this, and given a short series of tests, we realized that it would be extremely difficult to reach any conclusions about the relative effect of the fluxes upon refractory life.

Normal Practice ("SPAR")

The procedure employed for a normal heat using SPAR --- together with typical weights, etc. --- is outlined in Figure 1:

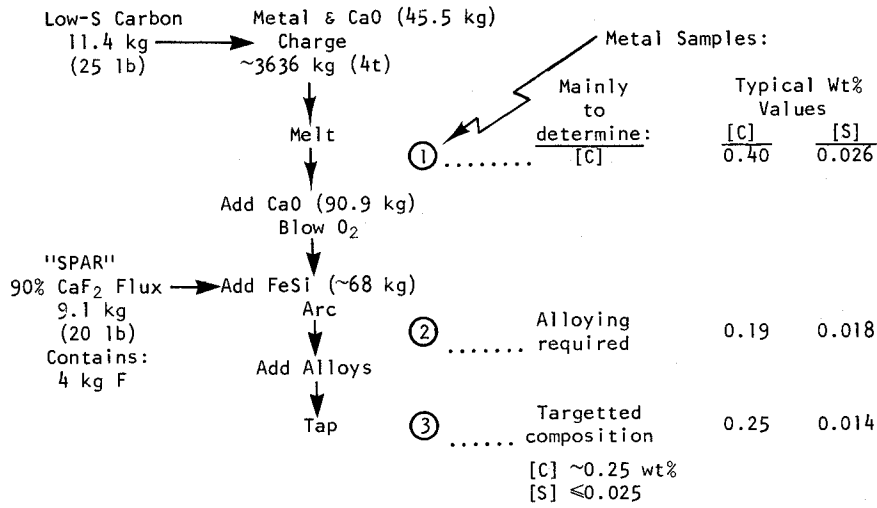


Figure 1. Normal Practice: C-steel ~4t Furnace

Briefly,

- The furnace is charged with scrap, lime and carburizer (a low-S carbon).
- The charge is melted and the metal is analyzed --- mainly to determine C-content.
- More lime is added and the melt is blown with oxygen --- to bring C-content into the ~0.25 wt% range and to purge undesirable gases from the melt.
- SPAR and ferrosilicon are added and heating is continued to a condition determined by the operator based on the appearance of the heat and the temperature, etc. The metal is now analyzed to determine the amounts of alloy ingredients to be added (to achieve the targetted final composition).
- Alloy ingredients are added, the melt is mixed, the temperature is adjusted, and the heat is tapped and killed. The metal in the ladle is now analyzed to ensure that it meets specification.

An important requirement, not yet mentioned, is that the S-content in the metal must be controlled. Thus, the final S-content in the tap must be ≤0.025 wt% --- and normally runs at about half this level. This S-content is critical --- and relates directly to overall slag performance. Typical C- and S-values are shown in Figure 1 for the given sampling sequence. The chemical composition of SPAR is given in Table 1.

Table 1
Furnace Materials

Material	Chemical Element, wt%							
	C	F	Na	Mg	Ca	Al	Si	S
SPAR	0.42	44.1	0.05	0.17	45.2	0.44	2.1	0.4
KARBRIK	29	12	14	0.1	3	11	0.7	0.1
KALBRIK	4	19	22	0.1	4	22	1.1	0.2

Lime: Na and Mg = 0.02 and <0.1 wt%, respectively.

Low-S carbon: S <0.1 wt%.

KARBRIK Practice

Because KARBRIK contains carbon (see Table 1), it is difficult to use this product as a direct substitute for SPAR (see Figure 1). This is because SPAR is usually added after C-content has been adjusted via the blow. However, realizing that carburizer was included in the charge, it was decided to investigate the possibility of putting KARBRIK into the charge where it would serve, perhaps, not only as a substitute for SPAR but also as a substitute for carburizer. It will be appreciated that this advances the introduction of flux in the melting procedure. As luck has it, the composition of KARBRIK is such that in adding KARBRIK in an amount sufficient to supply the normal amount of F (added with SPAR), we were simultaneously adding almost the normal amount of carburizer.

The furnace procedure using KARBRIK was changed along these lines, therefore --- to the protocol shown in Figure 2:

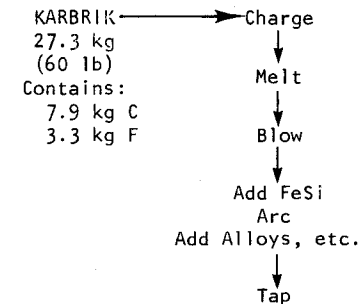


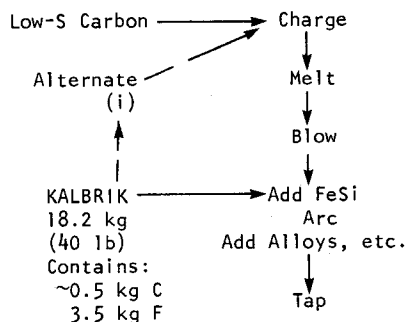
Figure 2. KARBRIK Practice (cf. Figure 1)

KALBRIK Heats

Because KALBRIK contains only a small amount of carbon (see Table 1), KALBRIK could be tested as a direct replacement for SPAR.

Alternatively, it was of interest to parallel the KARBRIK mode --- to see what differences, if any, would emerge as KALBRIK was fed into the initial furnace charge.

These routes are depicted in Figure 3:



(i) Alternate KALBRIK addition route to simulate KARBRIK practice (Figure 2).

Figure 3. KALBRIK Practice (cf. Figures 1 and 2)

Gas and Particulate Exit the Furnace

During each heat a considerable amount of gas and particulate is generated by the furnace. Most of this mixture is ducted away to a baghouse --- from which clean gas (mainly air) exhausts. The baghouse in this instance served both the 4-ton and a 10-ton furnace.

The amount and appearance of particulate generated in the furnace varies during the heat --- depending upon the instantaneous operation being carried out. Some particulate escapes the duct and leaks out into the foundry through the electrode ports and the door. This leakage is particularly noticeable during the oxygen blow.

Recognizing that the quantity and nature of the particulate could change with the flux, we decided to sample the particulate over the whole heat. Due to physical constraints, the only place where a particulate sample could readily be taken from the furnace duct, without building a massive scaffold, was located about 4 m off the floor, 5 m from the furnace and near a bend in the duct. A sampling port was, therefore, welded into the duct at this point.

Given this situation, we elected to take the particulate samples from that position in the duct's cross section determined by pitot tube measurements to be that having average gas velocity. Pitot tube traverses were,

therefore, made shortly after starting and finishing each heat and a specially off-set probe was used to reach the average velocity position. While this approach is not as accurate as traversing and sampling the duct at right angles at a location well-removed from any bend, it was believed that adequate measures of flow rate and fair samples would be obtained, and that the analyses of the samples would provide good relative comparisons between the compositions of the particulates.

The apparatus used to collect these particulate samples has been described (4).

Results

Metal

- In addition to normal runs using SPAR, about 25 and 15 heats have been conducted using KARBRIK and KALBRIK fluxes, respectively.
- All heats were within specification and all tapped metal was cast into product.

Table 2 shows no difference between heats using any of these fluxes in terms of tapped S-content.

It should be noted that the S-content of the C-SCC steel is:

- Much lower (by a factor of about 4) than for iron made in the USBM cupola (2). The difference stems from the use of a lot of relatively high S-content coke in the cupola.
- About the same --- though probably more consistently lower --- as that for steel made in the USBM BOF (3).
- The use of KARBRIK in a group of consecutive heats exhibited noticeable smoothness and uniformity of operation. The KARBRIK practice, of course, when viewed against normal procedure, eliminates one weighing and furnace addition (cf. Figures 1 and 2).

Table 2

Steel Quality: S-Content Tapped Metal

<u>Flux</u>	<u>S, wt%</u>	
	<u>Average</u>	<u>Standard Deviation</u>
SPAR	0.013	0.004
KARBRIK	0.012	0.003
KALBRIK	0.012	0.002

Approximately 10 heats in each case.

Table 3
Collection of Particulate Samples

Run	Flux	Addition Mode	Time (hr)	Particulate Sample (g)	Duct Gas Flow (sm ³ /sec) (a)	Total Run Particulate (kg) (b)
1	SPAR	Normal (Figure 1)	---	(c)	---	---
2			2.0	6.3	7.1	13.4
3			1.5	3.9	7.1	5.6
4			2.6	4.4	7.7	12.0
5	KARBRIK	To charge (Figure 2)	1.7	4.5	7.1	8.3
6	"	"	2.5	4.3	7.1	7.5
7	KALBRIK	Normal (Figure 3)	2.4	5.9	4.7	9.4
8			1.8	4.1	4.6	6.7
9			1.8	4.4	9.3	12.1
10		To charge (Figure 3 Alternate (1))	2.0	3.7	9.3	10.2
11		"	2.0	3.2	9.3	8.5

(a) Standard condition = dry air at 20°C and 76 cm Hg.

(b) Average = 9.4 kg. Standard deviation = 2.5 kg.

(c) Sample taken from baghouse (possibly slightly contaminated with KARBRIK particulate).

Particulate: Quantity

Details concerning the collection of particulate samples are given in Table 3:

These samples were worked up according to published protocol (4). The particulates were obtained as fine brown powders.

Early in this work, one particulate sample, closely representing normal SPAR operation, was obtained from the baghouse.

For any given run, the total amount of particulate, of course, is obtained from the weight of solid stripped from a measured volume of sample gas and the total flow of gas through the duct. The total particulate flows given in Table 3 range from 5.6 to 13.4 kg per heat. The main reasons for this spread are:

- Starting with a cold versus hot furnace
- Changing an electrode during a heat
- Waiting on the casting shop
- Running one or two furnaces on the same baghouse/fan system.

In addition, it should be recognized that while gas flow rate was measured on beginning and ending the melt, the instantaneous flow rate probably varied slightly during each heat. Moreover, as already mentioned, some gas (and particulate) escaped the duct by leaking into the foundry.

- The amount of total particulate generated during a heat is variable. The average value from Table 3 is 9.4 kg.

Particulate: Composition

Both wet and spectroscopic methods were employed to determine the chemical compositions of the particulate. The resulting data are given in Table 4.

- The most notable differences in the data are the greater concentrations of Na and F for KARBRIK and KALBRIK particulate compared with SPAR runs.

These differences are not too surprising because KARBRIK and KALBRIK contain more Na than SPAR (see Table 1), and Na compounds are somewhat volatile.

The length of time the flux resides in the furnace has a questionable effect on the amount of Na in the particulate, as noted by comparing Runs 5-6, 7-9 and 10-11.

- The USBM work also shows some Na volatility (2, 3).

Table 4

Composition of Particulate (wt%)

Run	Flux	Na	Al	Mg	F	Fe	Si	Ca	S	
1	SPAR	0.9	0.6	3.8	1.8	37	3	5	-	
2	↓	1.1	0.6	17.8	2.2	27	3	4	-	
3		1.5	0.4	2.8	2.4	40	3	3	-	
4		1.5	0.4	3.2	3.4	32	7	3	0.4	
5		KARBRIK	16.6	1.2	10.5	13.9	16	2	2	-
6	"	21.2	1.1	1.7	15.3	16	1	2	-	
7	↓	KALBRIK	7.0	0.6	4.1	6.4	27	5	2	0.9
8		9.5	0.6	6.3	5.8	22	3	4	1.0	
9		10.4	0.7	8.3	5.3	19	3	1	0.9	
10		(a)	5.7	0.5	12.9	11.8	16	3	4	0.7
11		(a)	3.6	0.5	5.7	10.7	28	3	3	0.5

(a) See Figure 3, Alternate (i).

Slag

The amount of slag generated in these runs was conservatively estimated to be 245 kg, based on the weights of slag-forming materials added to the furnace.

- In general, the slags obtained using KARBRIK and KALBRIK were more fluid than those obtained with SPAR.

The fluidity of potlining slags can be explained by the incipient presence of Na₂O, Al₂O₃, or sodium aluminate, and the various eutectics thereby formed (5). Improved fluidity was also observed by the USBM in their cupola and BOF tests (2, 3).

This effect is important for it implies that potlining flux could well prove effective in amounts containing less than equivalent F-content employed when using SPAR. Indeed, the USBM BOF tests show that potlining is effective at only about two-thirds the usual fluorspar (F-content) level.

- The chemical compositions of the slags analyzed in this study are given in Table 5. There appears to be little difference between these slags except for possibly:

- Slightly greater concentrations of Na and Al in KARBRIK and KALBRIK cases.

- Slightly reduced F-content in those instances where KARBRIK or KALBRIK were added to the initial charge.

- While, at one stage, we thought that the Mg-content of the slag (with the lime and other furnace materials containing little Mg) would provide information about refractory attack -- we quickly decided that this was a vain hope (see Test Heats; Refractory). No conclusions, therefore, can be based on the observation that the Mg-content of slags made using KARBRIK and KALBRIK are generally higher than those obtained using SPAR.

It is noteworthy that the USBM claims no difference in refractory attack (as measured by MgO-content in the slag) in both their cupola and BOF studies (2, 3).

Table 5

Composition of Slag (wt%) (a)

Run	Flux	Na	Al	Mg	F	Fe	Si	Ca	S	
1	SPAR	0.2	3.0	9.3	0.9	0.9	16	28	-	
4	↓	0.1	2.4	8.8	1.4	0.4	16	31	0.1	
6		KARBRIK	0.2	3.5	9.9	0.3	0.9	13	30	-
7	↓	KALBRIK	0.5	3.5	11.6	1.7	0.6	14	28	0.2
8		0.4	3.6	13.1	1.5	0.8	14	27	0.1	
9		0.4	4.9	15.9	1.1	1.5	12	22	0.1	
10		(b)	0.1	3.4	15.4	0.9	2.5	12	26	0.1
11		(b)	0.1	2.4	16.2	0.9	2.1	12	26	0.1

- (a) Slag reduced to powder in a shatterbox before analysis.
- (b) See Figure 3, Alternate(i)

Mass Balances

- Balances for Na and F can be calculated using the average amounts of total run particulate and slag produced in these heats, and their average compositions.

These balances are shown in Table 6.

- The high Na balance calculated for SPAR is probably due to contamination of the slag from previous KARBRIK runs.
- The low Na balance for KALBRIK Runs 10-11 may be due to the relatively low Na content of the slag compared with the other runs.

Table 6

Percentage Overall Balance (a)

<u>Flux</u>	<u>Na</u>	<u>F</u>
SPAR (b)	(d)	77
KARBRIK	83	55
KALBRIK	86	115
" (c)	25	95

- (a) Assuming zero contribution from refractory.
- (b) Assuming [Na] = 0, [F] = 43.8 wt %.
- (c) See Figure 3, Alternate (i).
- (d) High balance suggests contamination of slag by KARBRIK runs.

- These data may be presented in another form -- to show the percentages of Na and F retained in the slag. The data in Table 7 exhibit a range of values --- but indicate that these elements are well-utilized in these slags --- at levels much higher than in cupola and about the same as in BOF tests (2, 3).

Table 7

Percentage Retention of Na and F in Slag (a)

<u>Flux</u>	<u>Na</u>	<u>F</u>
SPAR	(c)	91
KARBRIK	25	39
KALBRIK	56	87
" (b)	36	68

- (a) Based on analyses of slag and particulate.
- (b) See Figure 3, Alternate (i).
- (c) Not calculated due to suspected contamination.

Conclusions

1. KARBRIK and KALBRIK -- as briquetted products made from spent potlining --- are used successfully as F-containing fluxes in place of SPAR in making alloy steel in a small electric arc furnace. This result is based on experiments using approximately the same amount of F in all cases.
2. Every one of the approximately 40 KARBRIK and KALBRIK heats was within specification (with fairly low S-content particularly important) and all of the tapped steel was used in making regular production castings.
3. KARBRIK -- containing ~30% carbon -- can be fed into the furnace charge where, in addition to replacing SPAR (usually added later in the heat), KARBRIK also replaces moderately low-S carburizer.
4. Slags produced by KARBRIK and KALBRIK appear more mobile than normal (when using SPAR) -- suggesting that less KARBRIK and KALBRIK may prove satisfactory. Recently-reported work by the USBM confirms this contention.
5. While there appears to be little difference in chemical composition between any of the slags, the particulate exhausted from the furnace using KARBRIK or KALBRIK contain increased concentrations of Na and F. The amounts of Na and F lost via this route, however, are relatively small --- for these components are well-utilized in the slag.
6. No conclusion can be made about the effect of KARBRIK or KALBRIK upon refractory life. Again, however, the USBM in related work has recently reported little, if any, adverse effect.

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Terms and Abbreviations

BOF	Basic Oxygen Furnace
KACC	Kaiser Aluminum & Chemical Corp.
CFT	Center for Technology (KACC)
CSCC	Columbia Steel Casting Corp.
KARBRIK KALBRIK	Briquetted products derived from spent potlining
SPAR	A commercial flux containing ~90% CaF ₂ .
USBM	U.S. Bureau of Mines

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