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CONTENTS

ILLUSTRATIONS

TABLES

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	lb/min	pound per minute
°C/h	degree Celsius per hour	p	poise
°F	degree Fahrenheit	pct	percent
g	gram	ppm	part per million
h	hour	rpm	revolution per minute
in	inch	scfm	standard cubic foot per minute
lb	pound	wt pct	weight percent

SYNTHETIC FLUORSPAR FLUX IN THE BASIC CUPOLA: EVALUATION OF OPERATION AND FLUORINE VOLATILITY

By H. W. Kilau,[1] V. R. Spironello,[2] I. D. Shah,[2] and W. M. Mahan[3]

ABSTRACT

The Bureau of Mines evaluated synthetic fluorspar as a substitute for natural fluorspar flux in basic cupola ironmaking. The synthetic fluorspars tested were prepared from waste fluosilicic acid generated during the processing of fluorapatite ore. The cupola trials showed the synthetic products to be the equivalent of natural fluorspar from an operational standpoint. However, wet scrubber sampling showed that substantial losses of volatilized fluorine occurred from the cupola during operation. The losses during synthetic fluorspar trials considerably exceeded those from natural fluorspar trials. Laboratory viscosity testing, using a high-temperature rotational viscometer, confirmed this finding and indicated that fluorspar volatility in slags is related to slag basicity. Synthetic fluorspar is accordingly recommended more for highly basic cupola operation (>1.3 basicity) than for neutral or acid operation, because of the increased potential for pollution and baghouse filter deterioration.

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[1] Research chemist.

[2] Metallurgist.

[3] Metallurgist (retired).

Twin Cities Research Center, Bureau of Mines, Minneapolis, Minn.

INTRODUCTION

This research is a continuation of work on synthetic fluorspars applied as a flux for iron and steelmaking operations (10).[4] This report covers synthetic fluorspar testing in cupola ironmaking operations and concludes the Bureau of Mines research on the metallurgical application of this material.

Fluorspar (CaF_2) is the predominant auxiliary flux employed in U.S. ironmelting and steelmaking operations. It is of concern to the Bureau of Mines because of its important role in the Nation's economy. The work is consistent with the Bureau of Mines goals to minimize the use of critical scarce commodities by substituting materials that are abundantly available in the United States.

Although fluorspar is not a major commodity in terms of annual production, it is critical for the aluminum, chemical, and steel industries of the world. Especially important is its use as a metallurgical flux, which represents over 60 pct of the world's fluorine consumption (14).

U.S. fluorine production fell below domestic demand about 30 years ago, resulting in a high reliance on foreign sources (over 80 pct of total U.S. consumption was imported in 1979). The fluorspar market is remarkably unstable; its supply-demand relationship is more easily affected than that of other mineral commodities (6). At the projected rates of consumption, all currently known fluorspar reserves will be depleted before the end of the century (2). By then, new fluorspar discoveries, lower grade fluorspar resources, and alternative fluorine resources, particularly phosphate rock, will have to be developed to satisfy U.S. and world demand. Interest in finding a suitable substitute for metallurgical-grade fluorspar was recently renewed by U.S. steelmakers owing to spiraling increases in the prices charged by the major world fluorspar suppliers in Mexico and the Republic of South Africa during 1979 and 1980. From a strategic point of view, it is advisable for the United States to begin reducing its dependence on foreign sources of fluorine-bearing materials. In the event of trade disruptions or embargoes, it is unlikely that alternative sources of fluorine could be developed in sufficient time to satisfy demand. The most promising alternative source is in the fluorapatite [$Ca_{10}(PO_4)_6F_2$] deposits in Florida and the Western United States. These deposits are currently being mined for their phosphate content for fertilizers, with only about 20 pct of the fluorine being recovered (15).

When phosphate ores are processed to make fertilizers or phosphoric acid, fluorine volatilizes as silicon tetrafluoride. To prevent air pollution, U.S. manufacturers collect the SiF_4 in water scrubbers where it is hydrolyzed to fluosilicic acid (H_2SiF_6), most of which is disposed as waste in storage ponds. The Albany (Oreg.) Research Center of the Bureau of Mines has been engaged in research to produce synthetic fluorspar for metallurgical applications by treating this waste fluosilicic acid with calcium compounds to precipitate calcium fluoride. Considering the low cost of the raw materials, the synthesis appears economically attractive. This material and a similar product produced by a domestic fertilizer manufacturer were evaluated for cupola ironmaking.

Fluorspar flux is added in the cupola ironmaking operation to ensure good coke combustion, increase carbon pickup by the metal from the coke, and prevent bridging. These benefits of fluorspar addition are derived from the lowered viscosity and liquidus temperature of the slag. The more fluid slag improves coke

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[4] Underlined numbers in parentheses refer to items in the list of references at the end of this paper.

combustion and carbon pickup through better removal of coke ash from the surface of the coke. Fluorspar is charged to the cupola in amounts ranging from 15 to 20 lb per ton of molten metal. The cupola can be operated satisfactorily without fluorspar if the slag has a basicity range[5] of 0.47 to 1.2, corresponding to acid and almost neutral slags (3, 17). However, operation in this range restricts the charge to more costly low-sulfur scrap if deleterious high-sulfur content in the iron product is to be avoided, particularly in the production of nodular or ductile iron.

If the cupola is operated at slag basicities above 1.3, a sulfur-refining capability is added to the slag's desirable properties. The higher basicity enables low-cost, high-sulfur scrap to be charged and improves carbon pickup to yield low-sulfur, high-carbon iron. The higher carbon results from the more effective removal of acidic silica ash from the coke by the basic slag, which then exposes more coke surface. In many cases the improved carbon pickup by the basic cupola permits 100-pct-steel charges to be used for producing good-quality gray iron (1). However, these highly basic slags are viscous and make cupola operations difficult from a practical standpoint. Such operation requires addition of fluorspar or other supplementary flux to maintain fluidity.

The synthetic fluorspars were evaluated using two methods:

1. The fluorspars received from the Albany Research Center and from the domestic fertilizer manufacturer were tested in the pilot plant cupola located at the Twin Cities Research Center (TCRC).

2. The fluorspars were tested in carefully controlled slag compositions and conditions in the TCRC viscosity laboratory.

The first method approaches actual industrial conditions but requires numerous, costly trials for judging flux performance accurately The second method measures a critical property (viscosity) of the slag under controlled laboratory conditions but may overlook important complications in the industrial cupola operation, such as changes in slag composition resulting from dissolved refractory. Together, the methods provide a means for making reasonably reliable evaluations of fluorspar substitutes. The report is divided into three parts: Part 1 covers the pilot cupola testing of the fluorspars, and part 2 covers the viscosity testing of simulated cupola slags containing the fluorspars, and part 3 discusses and compares the experimental results obtained from the cupola and viscometer testing.

ACKNOWLEDGMENTS

The authors wish to thank the Agrico Chemical Company of Donaldsonville, La., for providing one of the synthetic fluorspars used in this investigation.

PART 1.--EVALUATION OF SYNTHETIC FLUORSPARS IN BASIC CUPOLA

Two synthetic fluorspar substitutes were evaluated in the 18-in-diameter TCRC pilot plant cupola and compared with natural fluorspar.

MATERIALS

Two synthetic fluorspars were tested in the cupola. One material was obtained from the Bureau of Mines Albany, Oregon Research Center (ALRC). The second material was from a domestic fertilizer manufacturer (DFM). The ALRC synthetic fluorspar was prepared from scrubber water obtained from commercial phosphate

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[5] Basicity is defined in this report as the ratio of $\frac{CaO + MgO}{SiO_2 + Al_2O_3}$ in the slag with the component concentrations in weight percent.

operations. This water generally contains 18 to 24 pct fluosilicic acid (H_2SiF_6). The acid solution results when SiF_4 and HF vapors dissolve in water scrubbing units employed in conventional phosphoric acid and fertilizer manufacturing operations. The synthetic fluorspar was produced by precipitating CaF_2 through addition of $CaCO_3$ to the fluosilicic acid scrubber solution under controlled-pH conditions.

The DFM product was precipitated from cooling pond water (containing 1.3 pct fluosilicic acid) disposed as waste during the processing of Florida phosphate ore. Calcium carbonate was again used as the CaF_2-precipitating agent. Some of the details of this fluorspar synthesis were presented at the 1979 Fall Meeting of the American Chemical Society (4). Table 1 gives the chemical analyses of the two synthetic fluorspars and the natural (mineral) fluorspar used. The powdered synthetic fluorspar materials were pelletized without binder, while the natural fluorspar was added to the cupola in a crystalline pebble form. The DFM product had the greatest impurity content, particularly in sulfur and phosphorus, as indicated in table 1.

TABLE 1. - Chemical analyses of fluorspars tested in TCRC cupola, wt pct

Material	Natural (mineral) fluorspar	Synthetic fluorspar	
		Prepared by ALRC[1]	Prepared by DFM[2]
Fluorine..	45.0	44.3	40.0
Calcium...	49.9	47.1	37.9
SiO_2......	2.7	1.8	2.3
Phosphorus	.18	.58	2.3
Sulfur....	.25	.21	2.2
MgO.......	.2	NA	.5
Al_2O_3.....	.2	NA	2.4
Na_2O......	.1	NA	.9
Carbon....	.3	.2	NA
[3]CaF_2.....	92.5	91.0	82.2

NA Not analyzed.

[1] Albany Research Center, Bureau of Mines, Albany, Oreg.

[2] Prepared by domestic fertilizer manufacturer (DFM) from Florida phosphate ore.

[3] Calculated from fluorine content.

The cupola was charged with shredded automobile steel scrap for the fluorspar tests. The chemical analyses for the metal charged and other materials are given in table 2.

TABLE 2. - Chemical analyses of cupola charge materials

Constituents	Wt pct
Foundry coke:	
Fixed carbon..................	90.7
Moisture......................	<1.0
Volatiles.....................	.8
Ash...........................	8.3
Sulfur........................	.8
Limestone:	
Calcium.......................	39.2
Magnesium.....................	.4
SiO_2.......................	.2
Al_2O_3.....................	.7
Iron..........................	.3
Silicon manganese:	
Iron..........................	14
Silicon.......................	18.5
Carbon........................	1.5
Manganese.....................	65
Ferrosilicon:	
Iron..........................	50
Silicon.......................	48
Auto scrap:	
Iron..........................	97

EQUIPMENT

An 18-in-diameter cupola, used for all tests, had a well depth sufficient to provide about 300 lb of iron capacity. The combustion air was preheated to 600° F and distributed at 700 scfm to four 3-in-diameter tuyeres located 22 in above the iron taphole and 90° apart. Slag was tapped opposite from the iron taphole (back-slagging cupola, fig. 1). Exhaust gases generated during cupola operation were passed through a wet scrubber before exiting to the atmosphere.

PROCEDURE

After preheating the cupola and preparing the coke bed about 30 in above the tuyeres, the cupola was charged with steel scrap to provide a total of 330 lb

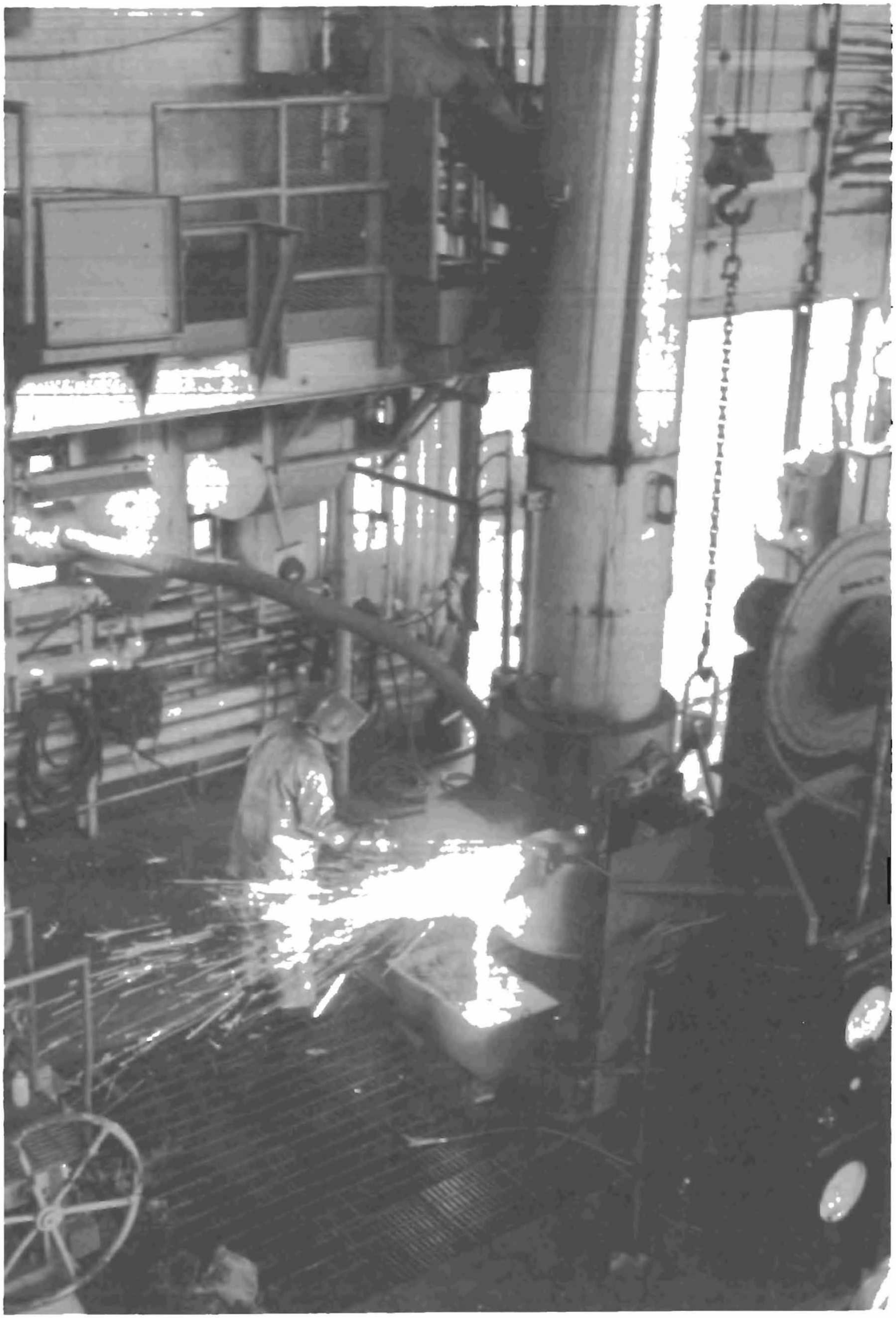

FIGURE 1. - Slag being tapped from TCRC cupola.

of iron for one tap. One trial of each fluorspar material was made (ALRC, DFM, and natural fluorspar); each trial consisted of seven taps. Limestone and ferroalloys were charged to provide desirable slag properties and metal chemistry. Coke was charged at a rate of 1 part coke per 5.5 parts ferrous charge. The charge makeup for all of the three trials is given in table 3. The molten iron was tapped into a ladle; iron samples were taken from the stream during three out of the seven taps, and the remainder were from the ladle. Slag was sampled from the stream on each of the seven taps of each trial.

TABLE 3. - Charge makeup for cupola trials[1]

Charge constituent	Weight, lb	Wt pct in total charge
Steel scrap...........	55.0	76.9
Coke..................	10.0	14.0
Ferrosilicon..........	3.0	4.2
Limestone.............	2.5	3.5
Silicon manganese.....	.5	.7
Fluorspar.............	.5	.7

[1]Each trial consisted of 42 charges.

EXPERIMENTAL RESULTS

Cupola operation was satisfactory for all the trials with no unusual skulling being noted; all slags had acceptable fluidity. Iron tapping temperatures were in the range of 1,293° to 1,455° C. The melting rates were 27.8, 27.1, and 26.8 lb/min, respectively, for natural, ALRC synthetic, and DFM synthetic fluorspar trials. The iron recoveries (weight percent of the metallic charge recovered as iron product) were 93.9, 97.5, and 94.6 pct, respectively, for the same three trials.

The chemical analyses of the irons and slags produced are given in table 4. The values shown are the averages of the constituents for the seven taps of each trial. The analyses of the iron products were all quite similar regardless of the type of fluorspar used in the slag. An examination of table 5, the chemical analyses of water and solids from the cupola's spray-type scrubber system, indicates that considerable fluorine is being lost to the gases exiting to the stack. The water analyses indicate that more fluorine was lost from the slag during synthetic fluorspar trials than from natural fluorspar. Although fluorine could be lost from disintegration of the pelletized synthetic fluorspars during charging, comparison of the fluorine analyses data for the solids does not confirm this explanation with complete satisfaction. The fluorine collected in the solids for the two synthetic fluorspar trials was not consistently greater than for the crystalline natural-fluorspar trial. The scrubber water fluorine analyses are believed to reflect the emission of a water-soluble, volatile fluorine compound from the slag during the cupola operation. This greater tendency of synthetic fluorspars to volatilize from molten slag agrees with the results of slag viscosity testing (to be discussed later) and with earlier work on BOF testing of synthetic fluorspars (10). However, the loss of fluorine was about 10 times greater during the cupola operation than in the BOF process, independent of the type of fluorspar used (synthetic or natural). The scrubber-water fluorine analysis for BOF testing (10) yielded only 26, 38, and 52 ppm fluorine, respectively, for tests of natural, ALRC synthetic, and DFM synthetic fluorspar. The laboratory viscosity testing of BOF and cupola slags also revealed greater losses of fluorine from the latter, indicating the losses were more a function of slag composition than a result of the metallurgical process.

TABLE 4 - Chemical analyses of cupola metal products and slags after synthetic fluorspar pilot plant trials, wt pct

Constituents	Natural fluorspar	ALRC fluorspar	DFM fluorspar
METAL			
Carbon	3.5	3.0	2.8
Silicon	1.9	2.3	2.1
Manganese	.63	.84	.75
Aluminum	<.005	.032	.02
Copper	.19	.32	.35
Tin	.026	.012	.012
Sulfur	.093	.074	.089
Phosphorus	<.01	.015	.027
SLAG			
Fluorine	0.6	0.6	0.48
Total iron	1.26	.9	.83
CaO	33.3	38.1	40.5
SiO_2	33.8	29.5	29.8
MgO	14.7	12.0	10.4
Al_2O_3	10.3	11.8	12.0
Sulfur	.55	.88	.9
Manganese	2.8	2.8	2.4

TABLE 5. - Chemical analyses of water and solids collected from spray-type scrubber[1] after cupola trials

Constituent	Natural fluorspar	ALRC fluorspar	DFM fluorspar
CHEMICAL ANALYSES OF WATER, PPM			
Fluorine	270	398	528
CHEMICAL ANALYSES OF SOLIDS, WT PCT			
Total iron	5.8	13.6	12.6
Carbon	NA	32.0	32.5
Al_2O_3	2.5	NA	NA
Manganese	.6	NA	NA
Copper	.22	.09	.13
Lead	.5	.59	.7
Tin	.64	.08	.12
Zinc	.8	1.34	1.2
Sulfur	NA	.76	.81
Fluorine	10.3	10.5	4.9

NA Not analyzed.

[1] The scrubber was a recirculating-type unit with the volume of water being maintained approximately constant for each trial.

PART 2.--VISCOSITY TESTING OF SIMULATED CUPOLA SLAG

The effects of synthetic fluorspars on slags of a composition typical of basic cupola operations were evaluated prior to the cupola trials. A laboratory high-temperature viscometer was used for this purpose. Viscosity testing of slags was found in earlier work (9, 17) to be a valuable aid in predicting the performance of fluorspar substitutes in both BOF and cupola operations.

MATERIALS

Two simulated cupola slags were prepared by first melting a mixture of major slag components (CaO, MgO, SiO_2, and Al_2O_3) to form a base slag. This base slag was ground to minus 100 mesh and modified by adding minor components (Fe_2O_3 and $MnCO_3$) and slightly adjusting the major components to give the slag the target compositions of table 6. The composition of slag 1 is a modification of a typical cupola slag selected from a reference book (2). The selected slag was modified by increasing the 7.8-pct-Al_2O_3 reference composition to 10.0 pct for ease of phase diagram analysis.

Earlier research (17) had questioned the necessity of adding fluorspar flux for cupola operation at slag basicities around the 1.0 neutral value. Therefore, slag 2 was prepared to evaluate synthetic fluorspar's fluidizing capability in a slag whose basicity most certainly required secondary fluxes to achieve adequate fluidity. Dvorak and Neuman (5), from their studies of viscosity data, concluded that operation of a cupola would be very difficult at basicities over 1.5 without supplementary fluxes. Cupola operation at high slag basicities is desirable for producing low-sulfur and/or high-carbon irons (1).

TABLE 6. - Target compositions of simulated cupola slags used in the viscosity testing of fluorspars, wt pct

	CaO	MgO	SiO_2	Al_2O_3	Total Fe	Total Mn	Basicity[1]
Slag 1.........	34.2	16.4	34.3	10.0	1.7	1.3	1.14
Slag 2.........	43.6	13.4	28.0	10.0	1.7	1.3	1.50

[1] Basicity is defined in this report as the ratio (CaO + MgO)/(SiO_2 + Al_2O_3) with the component concentrations in weight percent.

TABLE 7. - Chemical analyses of fluorspars used in viscometer testing of simulated cupola slags, wt pct

Material	Natural (mineral) fluorspar	Synthetic fluorspars		
		Prepared by ALRC[1]		Prepared by DFM[2]
		Product 1	Product 2	
Fluorine................	45.0	33.0	33.4	34.5
Calcium.................	50.0	41.9	40.0	40.0
SiO_2.................	3.1	.2	.2	.7
Phosphorus..............	.12	.30	.25	3.3
Sulfur..................	.07	.10	.09	2.2
MgO.....................	.2	.3	.3	.7
Al_2O_3...............	.03	.1	.1	1.8
Na_2O.................	.1	.1	.1	1.8
Carbon..................	.4	3.0	2.8	2.8
[3]CaF_2..............	92.5	67.8	70.7	70.9

[1] Albany Research Center, Bureau of Mines, Albany, Oreg.

[2] Prepared by domestic fertilizer manufacturer (DFM) from Florida phosphate ore.

[3] Calculated from fluorine content.

The fluorspars tested in the viscometer (table 7) were similar in preparation and composition to those tested in the pilot plant cupola, except for the synthetic fluorspar products from ALRC (products 1 and 2). These products contained considerable carbonate impurity, resulting in a lower CaF_2 content compared to the ALRC material used in the cupola trial.

EQUIPMENT AND PROCEDURE

The synthetic fluorspars were mixed with slags 1 or 2 and melted in a platinum-rhodium alloy crucible. The slag viscosity was measured and compared with that of similar slags containing natural fluorspar. The fluorspars were always added to give equivalent fluorine concentrations in the slag to eliminate any effects from differences in fluorspar product composition. Calcium and silica contents of the fluorspar materials were also taken into account when the slag mixtures of selected basicities were prepared.

The viscosity was measured with a high-temperature, rotating, concentric-cylinder viscometer as described in earlier work (9). A schematic diagram of the viscosity apparatus is provided in figure 2. In general, simulated slag and fluorspar flux were blended, sampled for chemical analysis, and melted in an air atmosphere in the Pt-Rh alloy crucible to a predetermined, constant volume. A Pt-Rh alloy spindle was immersed in the molten slag to a constant depth, and the melt was cooled from 1,500° C by a programed controller at a linear rate of 30° C/hr while the viscometer instrument rotated the spindle at 20 rpm. The instrument also sensed the resistance to spindle rotation (or viscosity); its analog output was connected to an x-y

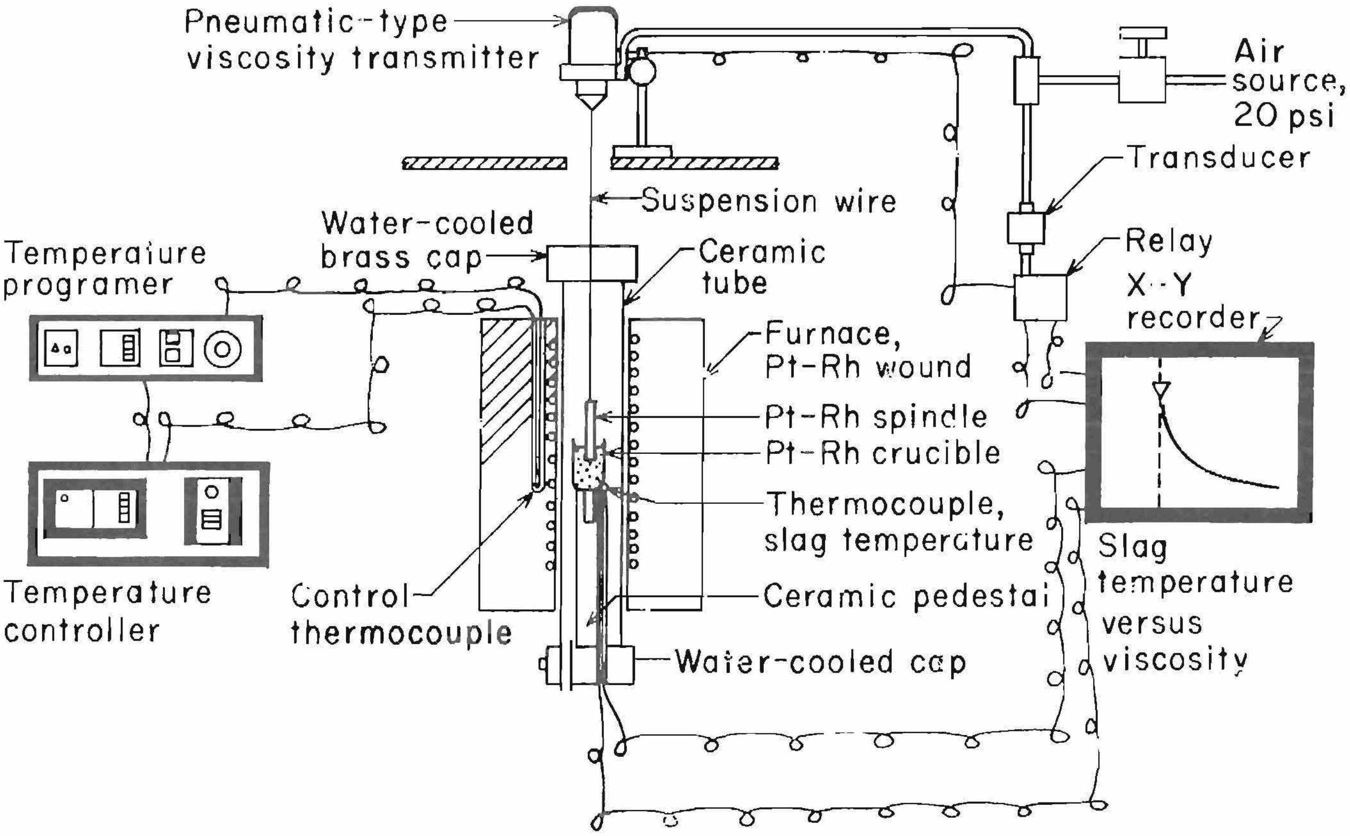

FIGURE 2. - Schematic diagram of viscosity apparatus

recorder. The recorder also traced the temperature of a thermocouple (6 pct Rh-Pt versus 30 pct Rh-Pt) in contact with the bottom of the crucible. Viscosity and temperature were recorded until the viscosity reached 85 p, at which point an automatic device stopped the spindle rotation to prevent damage to the suspension wire and instrument. The simultaneous plot of viscosity with decreasing temperature on the x-y recorder gave the characteristic L-shaped curve for basic slags, or a "viscosity" profile for the slag. The slag was remelted and heated to above 1,500° C, where cooling was begun to start a second traverse, and so on until the desired number of traverses was completed. All viscosity testing was done in an air atmosphere. After completing the viscosity testing, the molten slag was quenched in water and ground for chemical analysis. The reader is referred to reference 9 for further details on the operation and calibration of the viscometer.

EXPERIMENTAL RESULTS

Viscosity profiles were obtained for slags 1 and 2 before and after various additions of natural and synthetic fluorspars. Initial traverses for slag 2 after fluorspar additions showed some difference between the slag-fluidizing capabilities of synthetic fluorspar and natural fluorspar, but this result is likely due to differences in slag basicity. Subsequent traverses on both slags indicated that losses in fluidizing efficiency were due to volatilized fluorine. Slag basicity was an important factor controlling the fluorine volatility. Chemical analyses of the slags further supported the viscosity and cupola trial findings of relative fluorine instability in slag melts.

The viscosity profiles after the first traverse for both slags 1 and 2 fluxed with synthetic fluorspars are shown in figure 3. Curves A_1 through A_5 were obtained for slag 1, and curves B_1 through B_4 were obtained for slag 2. Curves A_1 through A_4, representing lower basicity slags with synthetic and natural fluorspar added, show very little difference in their viscosity profiles. Therefore, initially the synthetic and natural fluorspars have an equivalent ability to fluidize cupola slag in the 1.12 to 1.23 basicity range. Comparison was made on the basis of equivalent concentrations of fluorine in the slag, rather than the total amount of fluorspar material added. This treatment was necessary because of variability in the purity among the fluorspar products. Figure 3 also demonstrates the effectiveness of fluorspar, whether synthetic or natural, in reducing the viscosity of lower basicity slags (group A), as shown by the grouping of fluorspar-containing slags (A_1 through A_4) to the left (or more fluid side) compared to curve A_5, a slag without fluorspar flux. Figure 4 shows the viscosity profiles at the third traverse.

Each succeeding viscosity traverse for slags A_1, A_2, A_3, and A_4 reveals fluorine loss, as shown by the shifting of the viscosity profiles towards the right

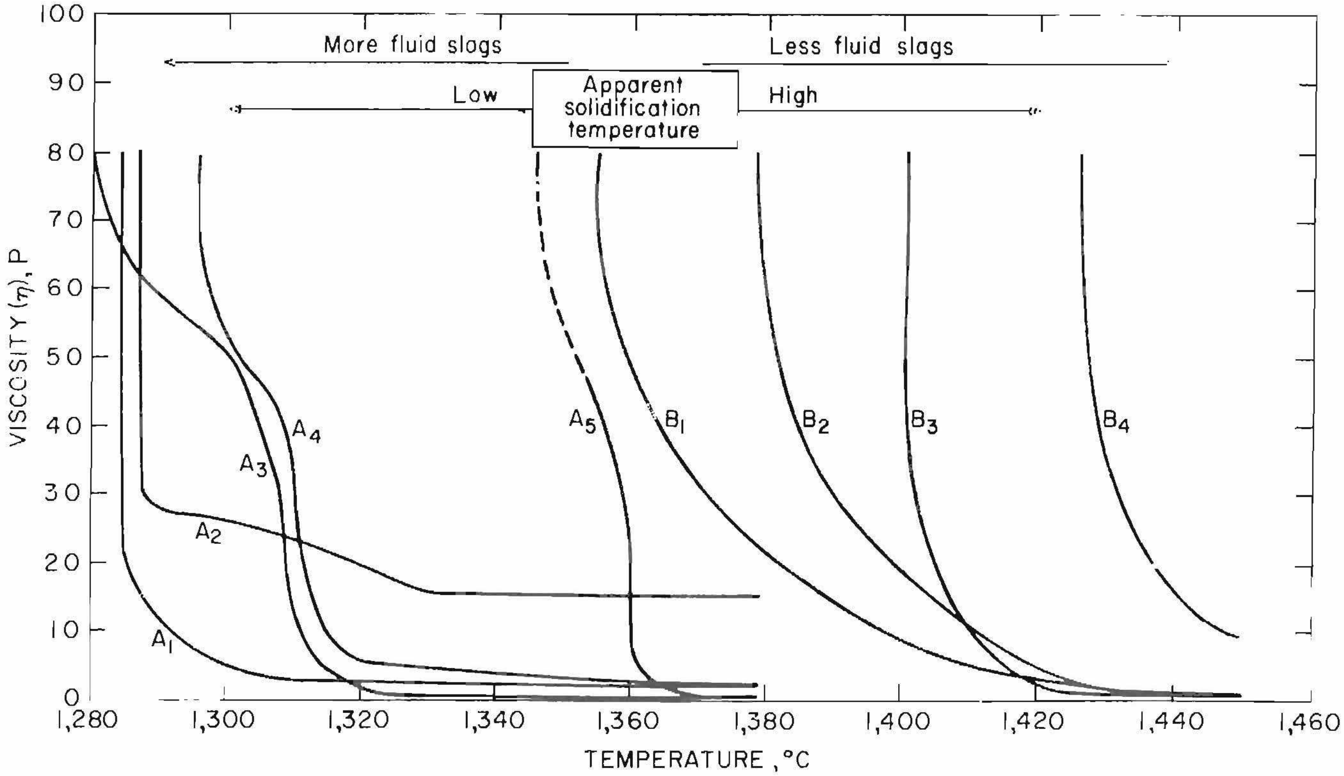

FIGURE 3. - Comparison of first-traverse viscosity-temperature profiles for simulated cupola slags. Fluorine concentrations given below are before viscosity testing. Curves: A_1—natural fluorspar, 1.9 pct F; A_2—synthetic ALRC, product 1, 1.8 pct F, A_3—synthetic ALRC, product 2, 1.9 pct F; A_4—synthetic DFM product, 1.5 pct F; A_5—no fluorspar; B_1—synthetic ALRC, product 2, 1.4 pct F; B_2—natural fluorspar, 1.4 pct F; B_3—synthetic DFM product, 1.3 pct F, B_4—no fluorspar.

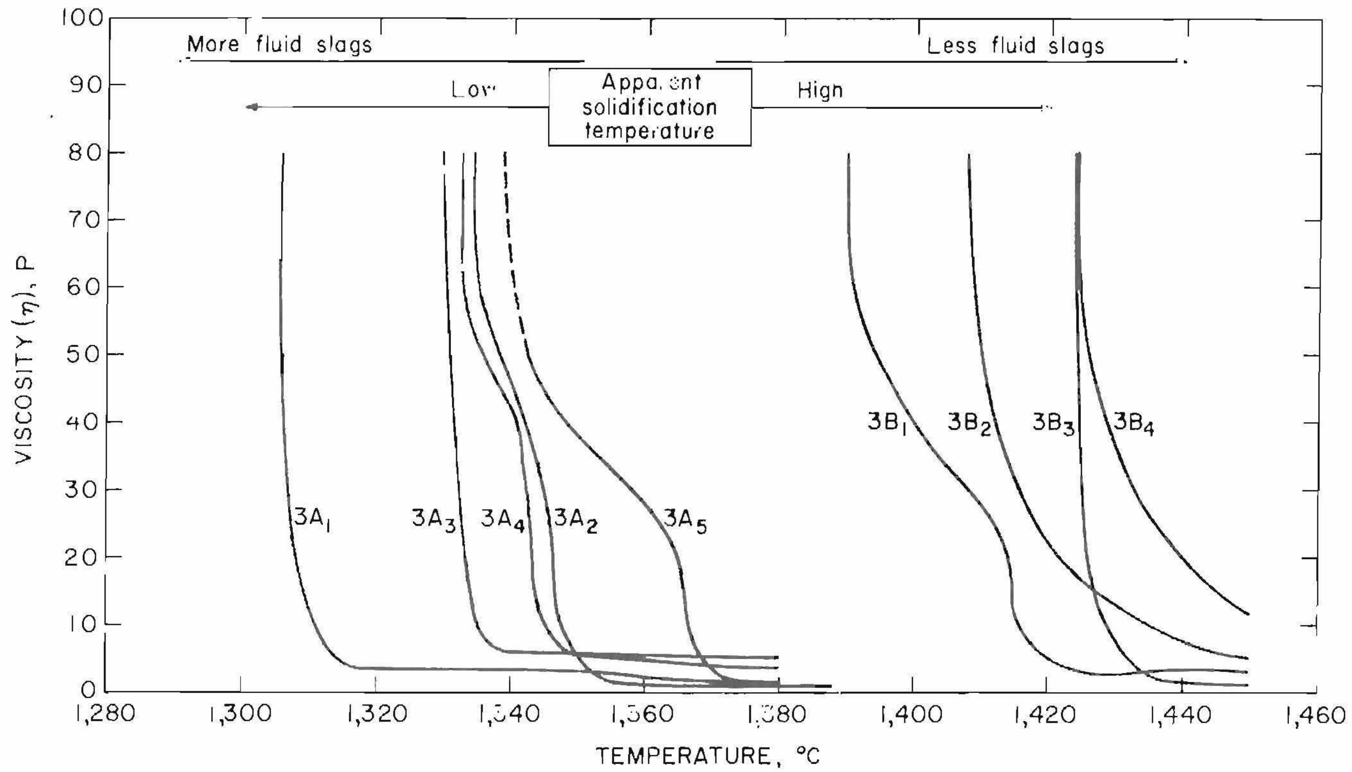

FIGURE 4. - Comparison of third-traverse viscosity temperature profiles for simulated cupola slags. Fluorine concentrations given below are after viscosity testing. Curves: $3A_1$—natural fluorspar, 1.5 pct F; $3A_2$—synthetic ALRC, product 1, 0.9 pct F; $3A_3$—synthetic ALRC, product 2, 0.7 pct F; $3A_4$—synthetic DFM product, 0.8 pct F; $3A_5$—no fluorspar; $3B_1$—synthetic ALRC, product 2, 0.8 pct F; $3B_2$—natural fluorspar 0.9 pct F; $3B_3$—synthetic DFM product, 1.0 pct F; $3B_4$—no fluorspar.

(less fluid side) as one goes from figure 3 to figure 4. Thus, the third traverse profiles ($3A_2$, $3A_3$, and $3A_4$), representing the same synthetic fluorspar slags of figure 3 (curves A_2, A_3, and A_4), have shifted to the right (less fluid side) and nearly coincide with the almost stationary curve $3A_5$, the lower basicity slag without fluorspar. The loss of fluorine in these cases has apparently been severe enough to render the slag fluidity to approximately the same condition as if no fluorspar had been added. On the other hand, curve $3A_1$ of figure 4 (natural fluorspar) has shifted much less to the right from its position in figure 3, indicating a significantly smaller loss of fluorine. This result correlates well with the results of the cupola trials. The fluorine losses are believed to be caused by volatilization of SiF_4 vapor or other volatile fluoride from the slag (7).

Viscosity profiles were developed for higher basicity cupola slag (slag 2) in the 1.30 to 1.43 range. In this range, supplementary flux would be definitely needed to achieve adequate slag fluidity. Such slags of higher basicity are desirable when melting high-sulfur metal charges, since the slag serves as a vehicle for sulfur removal as well as a coke ash flux and an antibridging agent. Figure 3 shows the viscosity profiles of slag 2 on the first traverse as the group B curves. These profiles show apparent differences in fluidizing capability between synthetic and natural fluorspars. However, because of the acute sensitivity of cupola slag to minor changes in the components that determine basicity, the result must be viewed with caution, as will be discussed later.

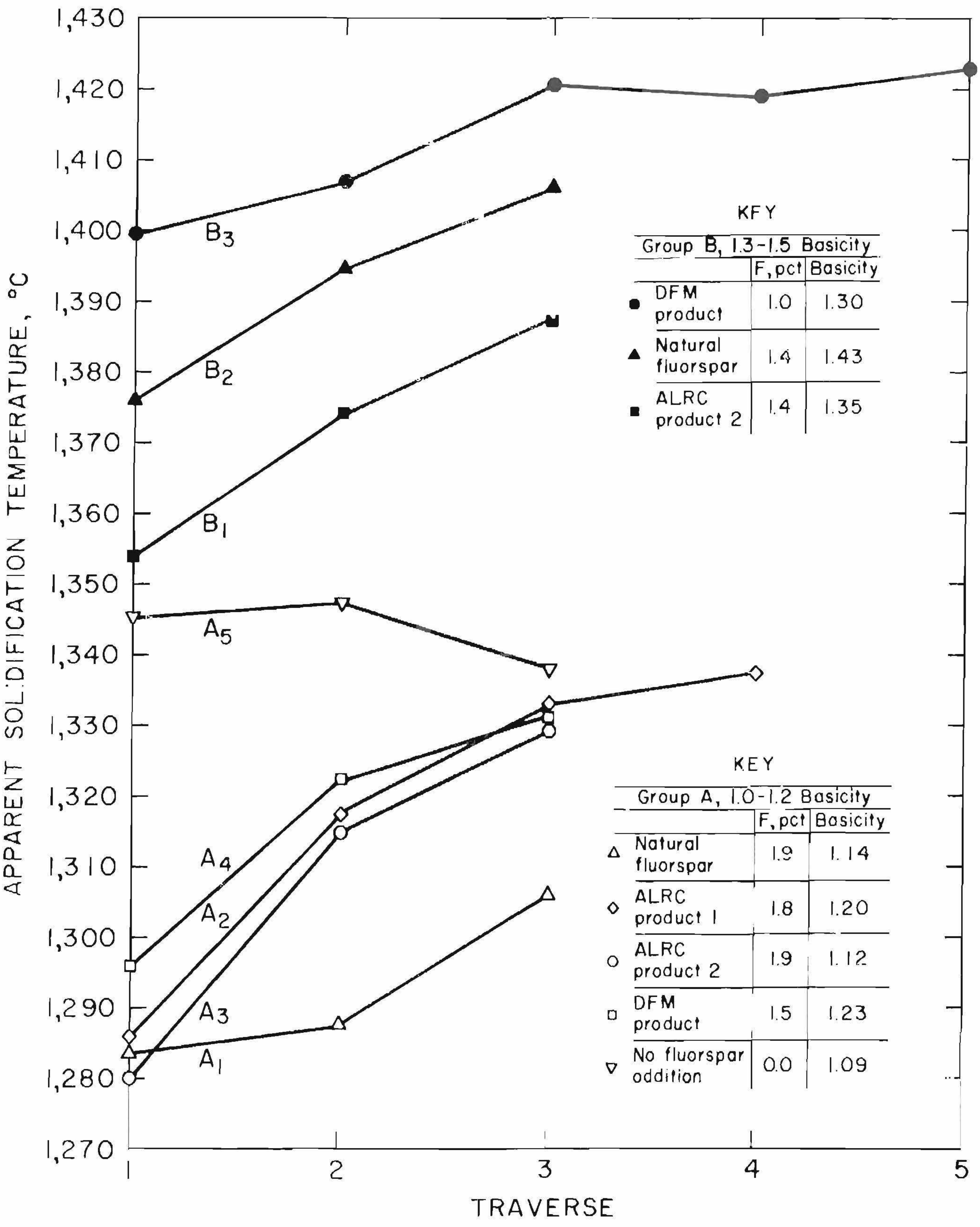

FIGURE 5. - Fluorine fade of slags estimated from increase in apparent solidification temperature with succeeding viscosity traverses. Fluorine concentrations in the slags are before viscosity testing.

The third-traverse profiles (fig. 4) for the B-group slags show similar fading to the right towards the stationary profile B_4 (slag 2 without fluorspar flux). However, unlike the A-group curves, the B-group shows a more uniform degree of fade independent of the type of fluorspar used. Natural fluorspar, in this case, does not exhibit superior fade properties. An alternative way to estimate differences in slag fluorine volatility is given in figure 5. The apparent solidification temperature (AST)[6] is plotted against the traverse number, and the fluorine loss can be inferred from the steady increase in AST on each subsequent traverse. Figure 5 demonstrates the differences in individual fluorspar performance quite well, but figure 6 illustrates the very significant dependence of synthetic fluorspar volatility on slag basicity. When the performance data from figure 5 and earlier BOF work (10) are plotted (fig. 6) so that traverse 1 for all experiments begins from the same point, a clear dependence of fluorine fade on slag basicity is revealed, particularly for the synthetic fluorspars. Since natural fluorspar slags tended to be less in accord with this analysis, the two viscosity experiments using natural fluorspar have been omitted from the figure for clarity.

This separation of fluorine-fade tendencies according to slag basicity is further supported by the analyses of the slags before and after viscosity testing. All the slags showed decreased fluorine concentrations after viscosity testing. The percent of the initial fluorine volatilized was calculated from the slag's fluorine and calcium analyses.[7] The fluorine loss percentages were averaged for each type of fluorspar, the averages were assembled into basicity groups, and a bar graph (fig. 7) was plotted. This figure shows a trend for lower basicity slags to volatilize fluorine more readily from their melts, which agrees with figure 6 and the results from the cupola operation. In addition, the intrinsic properties of synthetic fluorspar which lead to this volatility become more important when this material is used under lower basicity conditions.

A final specific test was performed to determine the influence of slag basicity on fluorine volatility. Synthetic fluorspar (DFM) was added in identical amounts

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[6] The apparent solidification temperature is defined in this report as the temperature at which the viscosity attains 80 p. Beyond this point the viscosity appears to increase infinitely with small decreases in temperature. This benchmark has been found helpful in earlier work (9-10, 17) when comparing viscosity profiles. Similar benchmarks have been cited by others (8, 12) as the preferred indicator of flux performance in basic slag.

[7] Calculated using chemical analysis for fluorine and CaO in the slag charge and products based on the conservation of CaO (CaO is assumed to be neither lost nor gained during viscosity testing). The formula is

$$\text{Percent loss} = 100\left[1.0 - \frac{(\%F_A)}{\%F_B}\,\frac{(\%CaO_B)}{\%CaO_A}\right],$$

where $\%F_A$ = percent fluorine in slag melt after viscosity testing,

$\%F_B$ = percent fluorine in slag charge before viscosity testing,

$\%CaO_A$ = percent CaO after viscosity testing,

and $\%CaO_B$ = percent CaO before viscosity testing.

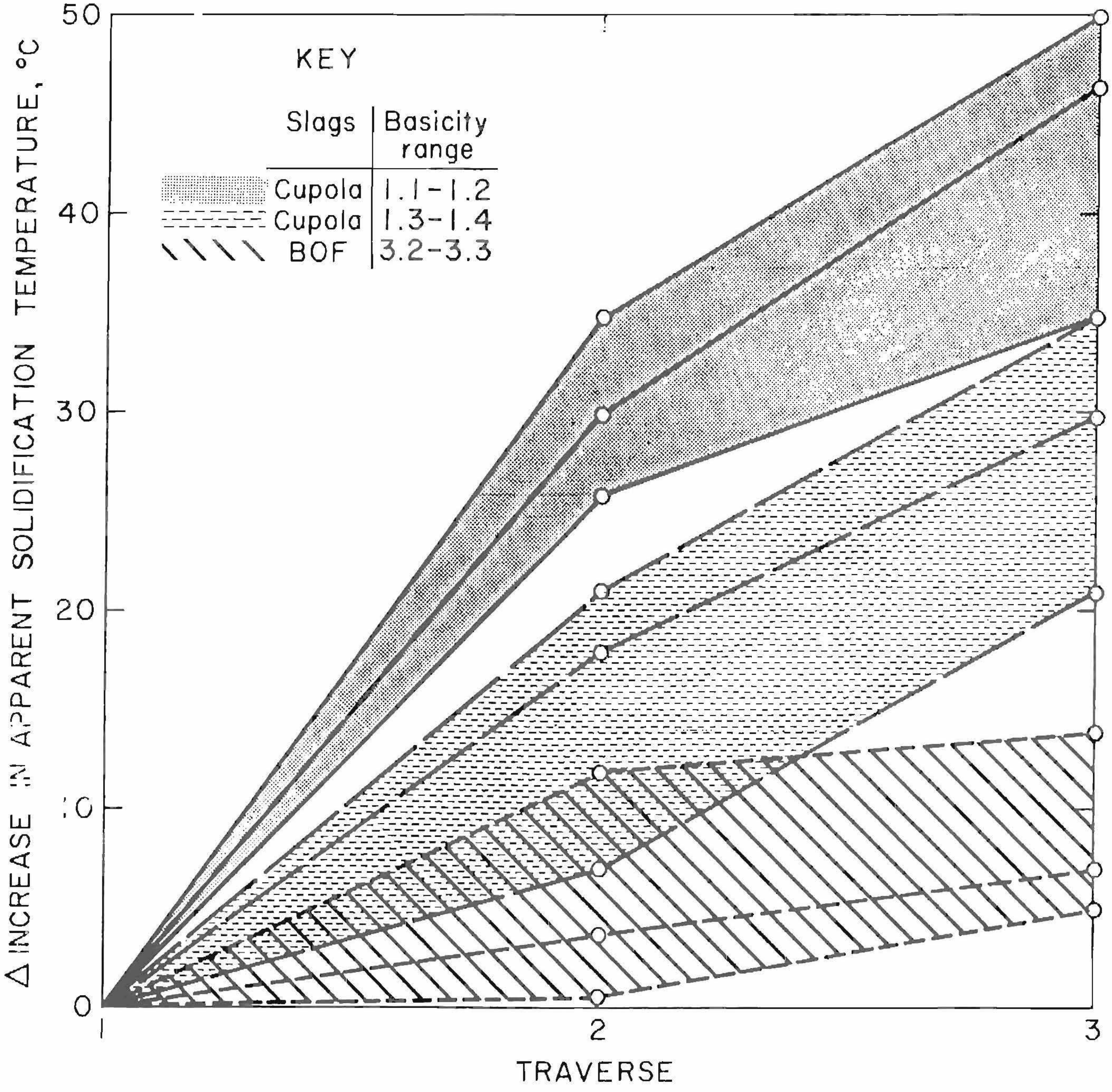

FIGURE 6. - Influence of basicity on the increase in apparent solidification temperature with each succeeding viscosity traverse, reflecting the loss of volatile fluorine compounds.

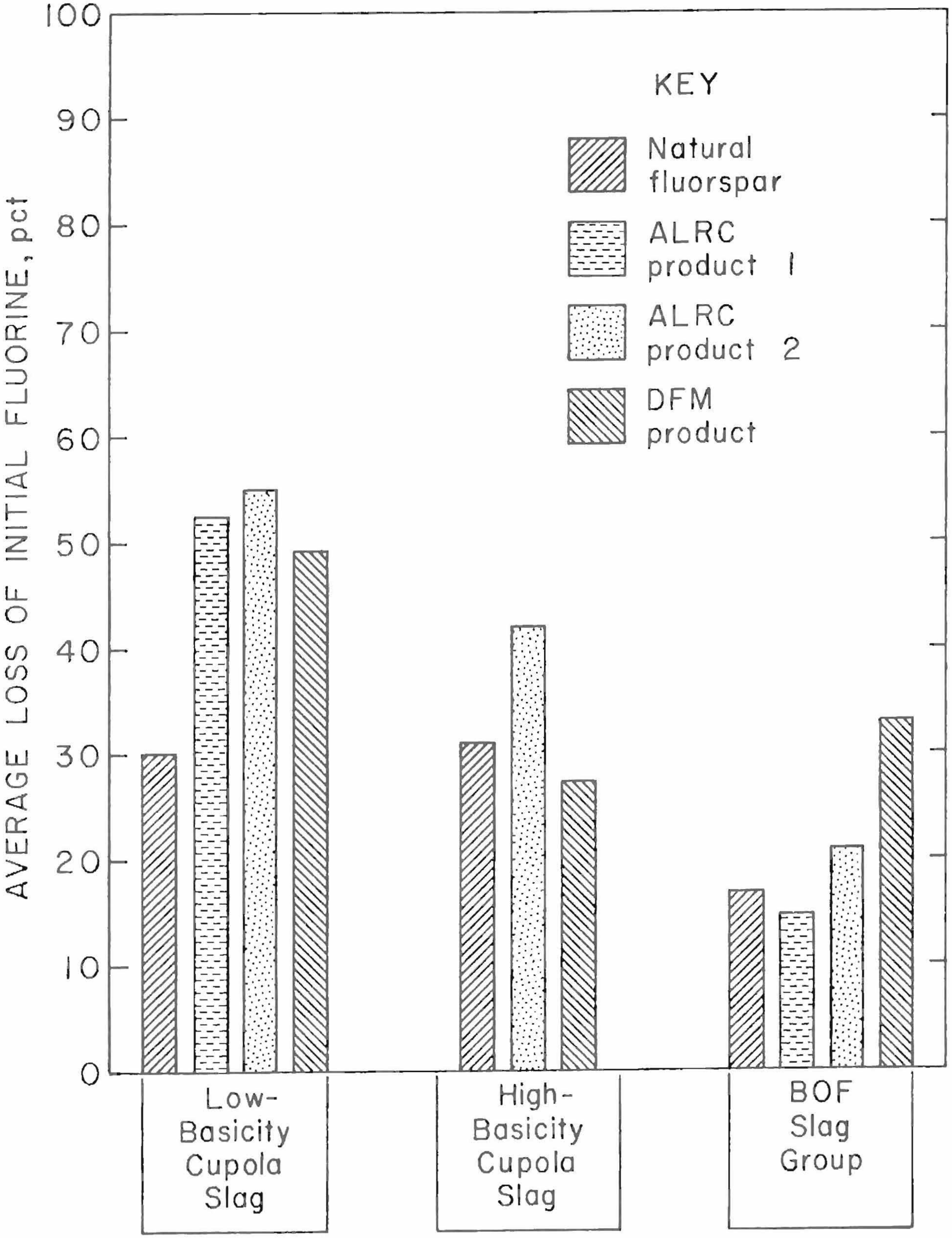

FIGURE 7 - Average fluorine losses from cupola slags and BOF slag after viscosity testing. Comparison of low-basicity (1.1-1.2) cupola slag, high-basicity (1.3-1.4) cupola slag, and BOF slag (3.0-3.3 basicity). Data were unavailable for ALRC product 1 in the high-basicity cupola slag group.

to low- and high-basicity cupola slags to give initial fluorine concentrations in the slags of about 1.2 pct. Exactly 40.0 g of each slag was melted in a Pt-Rh crucible at 1,480° C, held at this temperature for 24 h in ambient air atmosphere, and quenched by pouring on a cold steel plate. The two solidified masses were ground to minus 100 mesh and analyzed. The results, shown in table 8, reveal the remarkable effect a slight increase in basicity can have in retarding fluorine volatility. The fluorine loss is decreased 94 pct from the low-basicity value by merely increasing the basicity by an 0.26 increment.

TABLE 8. - Influence of cupola slag basicity on fluorine volatilization from slag melt

Slag	Basicity[1]		Fluorine loss, pct[2]
	Before melting	After melting	
Low-basicy...	1.10	1.05	48.1
High-basicity	1.36	1.25	2.8

[1] Defined as $(CaO + MgO)/(SiO_2 + Al_2O_3)$ with component concentrations in weight percent.

[2] Calculation based on the assumption that CaO is neither lost nor gained during the test, as was done for the construction of figure 7.

PART 3.--DISCUSSION OF CUPOLA AND VISCOMETER EXPERIMENTAL RESULTS

APPARENT SOLIDIFICATION TEMPERATURE

The mechanism by which fluorspar fluidizes basic slags is not clearly understood. Calcium fluoride is believed to break apart the polymeric silicate chains and networks that are thought to cause high slag viscosity in acid slags (11, 13, 16), but such silicate networks cannot exist in very basic slags owing to the formation of calcium silicates. Generally, basic slags containing fluorspar differ very little in their viscosities above the liquidus temperature, but when they are cooled they show variation in displacement of the "critical temperature" or "breakpoint" in the viscosity-temperature curve. The viscosity at this critical temperature increases infinitely with further decrease in temperature; the displacement is a function of the fluorspar in the slag. As fluorspar concentration is increased in the slag, the critical temperature decreases. Katz (8) concluded that flurospar's contribution to basic slag fluidization lies not so much in reducing viscosity but in shifting the critical temperature.

In the present investigation, evaluation of the fluorspars is primarily based on this critical temperature shift, or, in our terminology, the apparent solidification temperature. Katz also proposed that the critical temperature relationship was caused by a suspension of precipitated solid phase which has accumulated to about a 50-pct concentration in the slag. At a lower solids concentration, Katz believes that viscosity is relatively unaffected by the suspended solids. This property has been detected in other systems of suspensions of nonreactive, uniform, spherical particles. Precipitation of non-CaF_2-bearing crystallites is thought to occur first, causing CaF_2 to build up in the liquid portion of the slag, thereby reducing the further formation of solid phase with resulting decrease of the critical temperature. However, in contrast, Lanyi and Rosa's (12) evidence from viscosity and X-ray diffraction measurements of continuous-casting slags led them to an opposite view. They suggest that CaF_2 tends to accumulate in the crystallites, impoverishing the remaining liquid of the fluorspar fluidizer. This causes the abrupt, asymptotic viscosity increase which they labeled the "breakpoint".

ERRORS ARISING FROM SLAG BASICITY VARIATIONS

Evaluation of the performance of fluorspar substitutes in cupola slags is difficult because of errors resulting from comparatively slight changes in slag composition. The difficulty in reconciling viscosity profiles between pilot plant cupola slags and simulated slags was noted in earlier work (17). The discrepancies in that work came from increased MgO in the cupola slags, a consequence of the erosion and dissolving of the cupola lining.

The problem with accurate comparison of cupola slag viscosity profiles and observations of cupola operation is shown in figure 8. The apparent solidification temperatures of a number of slags containing no supplementary flux are plotted as a function of their basicities, as determined by chemical analysis. The data in figure 8 include both pilot plant cupola slags and simulated slags without fluorspar or any other supplementary flux, measured routinely over a period of time in the TCRC viscometer laboratory.

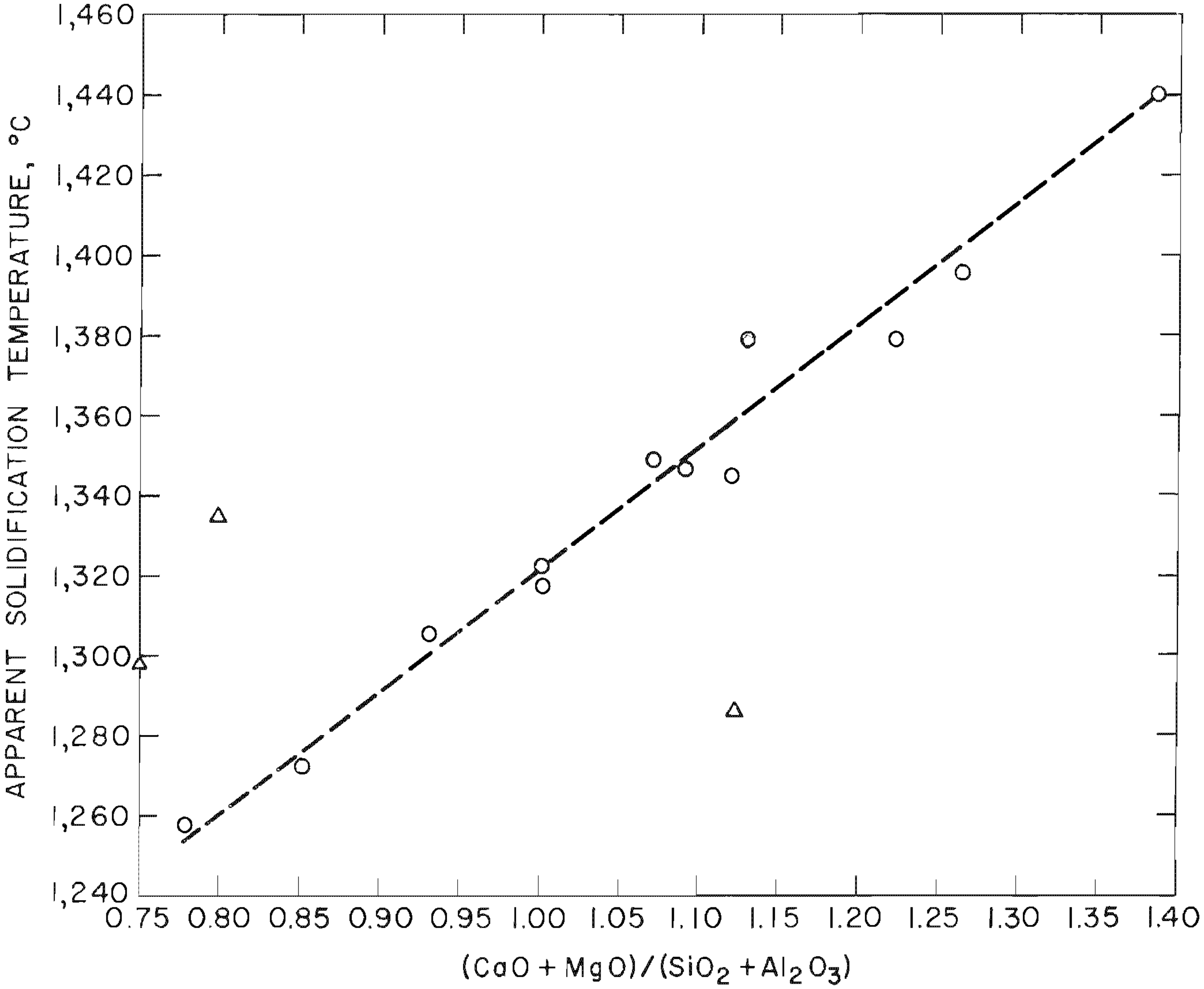

FIGURE 8. - Apparent solidification temperature as a function of slag basicity, no fluorspar or other supplementary flux present.

The data represented by the circles in the figure tend to be linear in the basicity range studied (0.75 to 1.4). These points fall within the slag composition ranges 28.3 to 39.8 pct CaO, 8.0 to 19.0 pct MgO, 29.5 to 37.3 pct SiO_2, 8.8 to 12.7 pct Al_2O_3, 1.1 to 2.4 pct total iron, and 0.8 to 2.4 pct total manganese. The triangles in the figure represent slags outside these ranges, which may explain their large deviation from the rest of the data. Thus, in two cases, the Al_2O_3 contents (16.5 and 23.7 pct) considerably exceeded the composition range, while the third case had higher iron content than normal. A linear regression analysis of the data (circles) in figure 8, omitting the data falling out of the stated composition range (triangles), yielded the straight line defined by the empirical equation:

$$A = 301\ B + 1020$$

where A = apparent solidification temperature in °C,

and $B = \frac{(CaO + MgO)}{(SiO_2 + Al_2O_3)}$ or basicity.

This equation is estimated to be capable of predicting the AST of a given cupola slag (containing no supplementary flux) within ±15° C maximum error (90-pct confidence level) when applied to normal cupola slags of the composition and basicity range indicated. This relationship, if valid, may be useful as a guide in slag preparation and adjustment for cupola operations. However, it is likely applicable only in this narrow basicity range, apparently located on a linear portion of the concave-upward curve that would be formed if the AST values were determined and plotted to include extreme basicities, both low and high.

If the empirical equation above is used to interpret the group B, higher basicity viscosity profiles of figures 3 and 5, the apparent differences between the curves become less significant. Thus, curves B_1 and B_2 in figures 3 and 5 have AST values over 20° C apart, despite identical fluorine concentrations (1.4 pct). However, their basicities (1.35 and 1.43), when substituted into the empirical equation, give predicted AST values of 1,427° and 1,452° C, or 25° C apart. That value is sufficient in itself to cause the recorded AST difference, so the nature of the fluorspars need not be involved. The sensitivity of the cupola slags to minor differences in composition approaches the errors involved in the viscosity measurement, the chemical analyses of the slags, and the variation of volatilized fluorine to be expected during slag heat-up to the molten state for viscosity measurement. Therefore, unlike the earlier work with BOF slags, which did not show such sensitivity, there is considerable hazard in relying greatly on individual viscosity profiles of cupola slags. This source of error from slight basicity differences is even more of a problem in evaluating actual cupola performance of a fluorspar substitute, where large changes in slag composition are likely to occur. The many contradictions in the literature as to the efficacy of these substitutes may find their origins in this error source. To avoid possible error through overextending the data, it is advisable to have several sources of experimental evidence when evaluating fluorspar substitutes for cupola operation.

FLUORINE VOLATILITY

The dependence of fluorine volatility on slag basicity was revealed in viscosity testing (fig. 6), chemical analyses (fig. 7 and table 8), and the comparable data from collected cupola and BOF scrubber waters (table 5). The evidence that fluorine volatility is increased in silica-rich slags supports the idea that the volatile fluoride compound expelled is a silicon fluoride such as SiF_4. The greater thermodynamic activity of silicon oxides in the lower basicity (silica-rich) slags may increase the potential for combination with fluorine to form a volatile silicon fluoride.

As mentioned earlier, Lanyi and Rosa (12) suggest that the viscosity breakpoint for basic slags originates from the precipitation of small crystallites from the liquid phase, where the crystallites extract the fluorspar fluidizer from the molten liquid. They detected the presence of fluorides such as CaF_2 and cuspidine ($Ca_4F_2Si_2O_7$) in precipitated crystallites by X-ray diffraction. If their proposal is correct and is applicable to cupola slags, it may explain the suppression of fluorine volatility in higher basicity slag. Fluoride in higher basicity slags may separate from the molten liquid phase by accumulating in the solid phase (crystallites) in a relatively nonvolatile form. That would diminish its reaction with silicon oxides in the liquid phase, and supress volatile silicon fluorides.

It is not clear, however, why synthetic fluorspar is particularly susceptible towards forming volatile silicon fluorides. X-ray diffraction examination revealed no significant differences in crystal structure between synthetic and natural fluorspar. Early synthetic fluorspar products tested showed greater thermal instability compared to natural fluorspar when they were heated overnight at 1,000° C in the absence of slag (10). Later products (the ones used in the present work) were improved to the extent that their thermal stabilities in the absence of slag were equivalent to or better than that of natural fluorspar. Yet the apparent greater instability persisted when the products were melted in contact with slag.

Perhaps it is more accurate to consider the improved synthetic fluorspars as being more reactive towards silicon in slags, rather than as relatively unstable. The origin of this greater reactivity is unknown. An understanding of this behavior could lead to preparation of improved, pollution-free fluxes. As a consequence of the greater volatility of synthetic fluorspar in low-basicity cupola slags, the cupola operator can expect a greater burden on pollution-prevention equipment. Fiberglass baghouse equipment, particularly, would be subjected to greater destruction from the HF formed by reaction between moisture in the air and the volatilized fluorides. Therefore, it is not desirable to use synthetic fluorspar in low-basicity (1.0 to 1.2) cupola operation or for acid operations. For operation at higher basicities (greater than 1.3), where sulfur removal is a consideration and supplementary flux is definitely required, synthetic fluorspar appears to be quite viable as an alternative to natural fluorspar. The higher basicity should help reduce fluorine emissions and eliminate the need for ladle desulfurization of the iron product.

CONCLUSIONS

The principal problem revealed in testing synthetic fluorspars for cupola operation was that of excessive fluorine emissions, particularly from low-basicity slags. Hence, synthetic fluorspar is recommended more for highly basic cupola operation (<1.3 basicity) than for neutral or acid operation, because of the increased potential for pollution and baghouse filter deterioration. All fluorspars tested were otherwise satisfactory from a cupola operation standpoint.

The fluorspars appeared to have different fluidizing capabilities towards higher basicity (1.3 to 1.5) cupola slag, according to initial viscosity profiles. But, because of errors originating from slag basicity variation, apparent differences in fluorspar's fluidizing ability could not be judged with certainty.

Lower basicity (1.0 to 1.2) cupola slags showed little difference in slag-fluidizing ability until subsequent viscosity traverses. The fluidizing power of synthetic fluorspars in lower basicity slags decreased at a faster rate than that of natural fluorspar on subsequent traverses, a consequence of fluorine loss through volatilization. In general, apparent fluidizing differences between fluorspars (with identical initial fluorine concentrations in the slag) are the result of variable volatility rather than of some other intrinsic difference in the fluorspars.

Considerable evidence in this work indicates greater reactivity of synthetic fluorspars (compared to natural fluorspar) towards the silicon atoms present in lower basicity slags, such as cupola slags, compared to high-basicity slags, such as those used in BOF steelmaking. Further research to understand this behavior could lead to improved fluorspar fluxes possessing greater fluorine stability.

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