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Electrolytic Reaction

The electrolytic vessel was a covered graphite crucible, 4½ in. deep, 5 in. ID with ½ in. walls in a closely fitting steel shell in a furnace (Fig. 1). The electrolyte was 10 g of aluminum and 270 g of bath [84.3% cryolite (3NaF·AlF<sub>3</sub>), 9% CaF<sub>2</sub>, and 6.7% Al<sub>2</sub>O<sub>3</sub>]. A thermocouple

Reaction Between Carbon Lining and Hall Bath

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Abstract

Sodium diffused rapidly into carbon lining during electrolysis of Hall bath. The rate increased with increasing current density. In the absence of current, sodium that is dissolved in molten aluminum diffused into carbon. Diffusion took place chiefly in the binder coke. Of the vapors that might exist over Hall bath, only alkali metals and calcium reacted with carbon to cause swelling. Carbon linings in Hall cells graphitized with age. In short-term tests bath vapors did not react with graphite.

Introduction

Smelting cells for aluminum production by electrolysis of alumina dissolved in molten cryolite (Hall bath) generally are lined with carbon made by baking a mixture of coal-tar pitch and anthracite. During operation bath constituents are lost into the lining, which at the same time expands and eventually cracks.

Rapoport and Samoilenko<sup>1</sup> measured expansion of lining materials during electrolysis. They found expansion to be increased by use of petroleum coke in place of anthracite, by decreased temperature, or by increased ratio of NaF to AlF<sub>3</sub> in the bath. Increased amounts of CaF<sub>2</sub> in the bath or graphite aggregate decreased expansion. Sodium vapor absorption paralleled the expansion results. Aluminum carbide formation did not cause expansion. High current density increased initial rate of expansion but did not affect the ultimate value. Applied stress decreased expansion in the direction of application. A recent Russian treatise<sup>2</sup> interpreted rate of bath absorption in terms of pore sizes in lining.

The work reported here describes the effect on carbon lining of (a) electrolytic reaction, (b) bath vapors, and (c) graphitization.

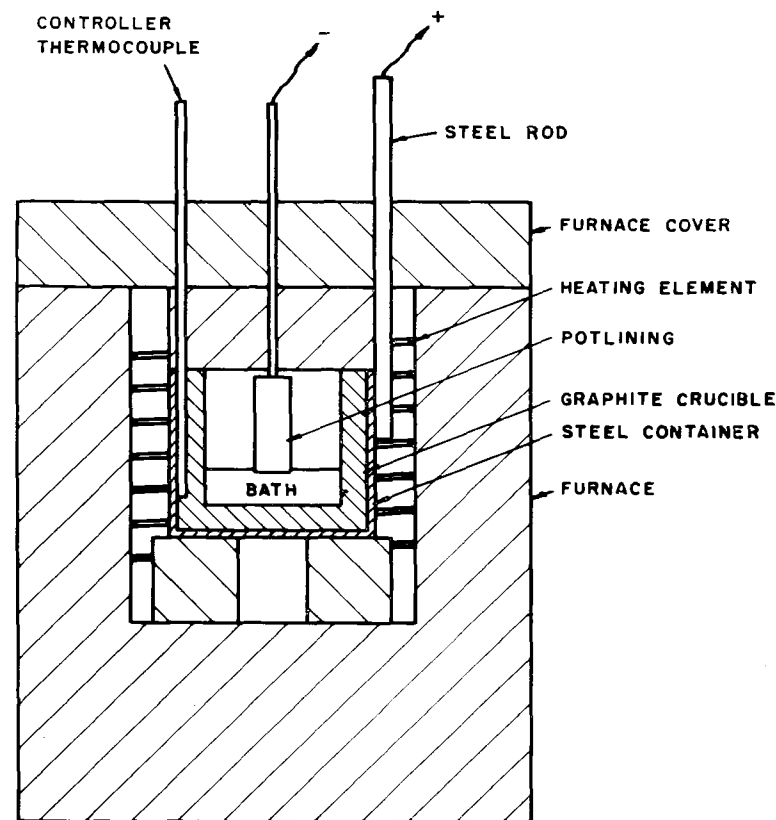


Fig. 1. Electrolysis apparatus.

between the crucible and the steel shell was ordinarily maintained at 970°C by a temperature controller. The graphite crucible was the anode. The cathode was a cylinder of carbon 1 by 3 in. long dipping into the bath and supported by a threaded steel rod.

In a second type of electrolysis to simulate a reduction cell, the 1-in. diam cathode was cemented with pitch into the bottom of a Refrax

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TABLE I  
Reproducibility of Diffusion Test  
(968°C, 5 amp/in.<sup>2</sup>, 6 hr)

Distance from bottom, in.	Sodium, % of sample	
	Run 15	Run 16
0.09	8.04	8.35
0.28	8.59	8.90
0.47	7.04	7.73
0.66	3.68	6.12
0.85	1.61	2.28
1.03	0.66	1.15
1.22	0.24	0.42
1.41	0.12	0.18
1.60	0.07	
Untreated	0.02	0.01

(silicon nitride-bonded silicon carbide) crucible, the top surface being flush with the bottom of the crucible.

Carbon specimens were molded at 6000 psi from a hot mixture of baked (1000°C) anthracite (7% ash content) with 13% of pitch binder. The binder consisted of a 1:5 ratio of pitches having softening points of 110°C (cube in air) and 40°C (cube in water), respectively. After baking at 1000°C for 24 hr, specimens had an apparent density of 1.400 g/cu cm, a real density of 1.856 g/cu cm, and a calculated porosity of 24.5%.

Carbon specimens were lowered 1/16 in. into the molten bath and electrolysis was started with current density maintained usually at 5 amp/sq in. At the end of a run (usually 6 hr), each sample was quickly placed in a covered crucible and cooled in a desiccator. Discs were cut from the specimen representing successive 3/16 in. intervals from the bottom. A sample equal in weight to one half that of the disc was punched from its center and analyzed.

Reproducibility of diffusion measurements (Table I) was excellent—especially near the bottom of the specimen. It was not good, however, between specimens from different laboratory batches. Two batches were used: the first batch up to and including run 5, the second for all succeeding runs.

**Results**

Sodium was the chief constituent diffusing into carbon (Fig. 2). From the shape of the curve it is apparent that sodium diffused in two

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waves, the second wave extending about 1 in. The break in the curve was not due to a temperature effect. The inside temperature of a longitudinally drilled specimen did not differ from the bath temperature by more than two degrees at a point 1.2 in. from the bottom of the carbon. The first wave of sodium was uncombined, as shown by absence of fluorine beyond the 1.2-in. level. Aluminum declined rapidly to 2%, the amount in the untreated carbon. Calcium diffused at a steady rate and then declined to zero. Silicon, iron, and titanium, which were originally present in the anthracite, were volatilized as salts during electrolysis.

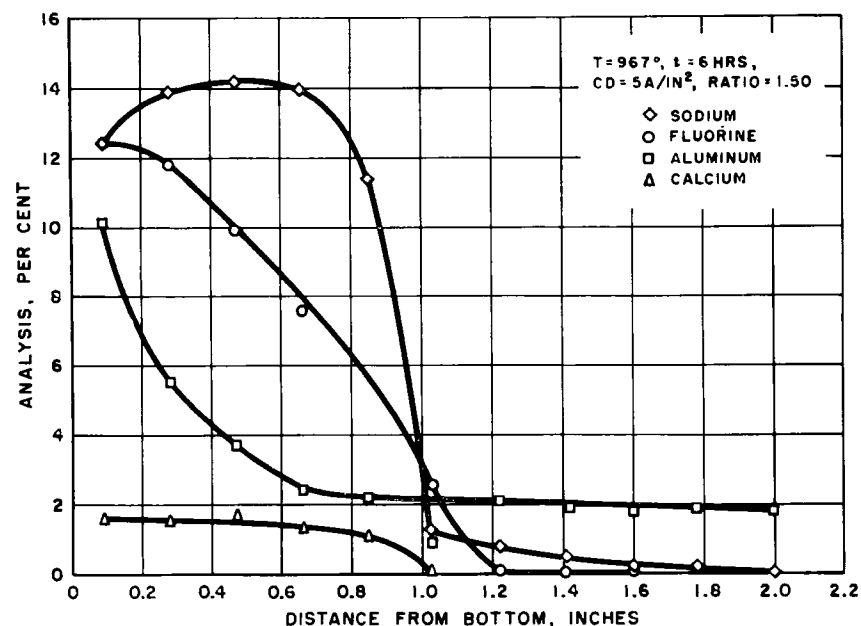


Fig. 2. Bath constituents absorbed by carbon, run 1.

When the carbon extended through the bottom of a nonconducting crucible into a 1-in. pad of aluminum between bath and carbon, there was less diffusion into the specimen than in run 1, where the carbon dipped into the bath (Table II). Relative diffusion of various species 0.28 in. from the bath interface, however, was not affected by specimen position, as shown by the analysis on an atom per cent basis.

The effect of increased time of electrolysis (Fig. 3) was to advance the zone of high absorption of bath constituents. For carbon under a 2-in. aluminum pad (Fig. 4), sodium diffused well beyond 1 1/2 in. in 24 hr.

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TABLE II  
Diffusion into Vertical Cathodes above and below Bath

Cathode position	Run	Distance, in.	Na	F	Al	Ca	Si	Ash
Analysis, Wt-%								
Above	1	0.28	13.9	11.8	5.5	1.5	1.2	40.7
Below	2	0.28	5.3	4.5	3.0	0.5	1.6	21.4
Above	1	0.85	11.4	6.3	2.2	1.1	1.6	20.5
Below	2	0.85	0.2	0.2	1.1	0.1	1.0	6.1
Analysis, Atom-%								
Bath compn.			28.6	51.9	14.8	4.8		
Above	1	0.28	43.4	44.6	9.5	2.5	--	--
Below	2	0.28	43	44.2	10.4	2.2	--	--

A tracer experiment like run 1, but using radioactive sodium, demonstrated that sodium diffused initially into carbon chiefly through the porous coke formed from pitch binder and not through the relatively nonporous anthracite. The autoradiogram is shown in Figure 5, dark areas indicating radioactive sodium.

For the same number of faradays (Fig. 6) diffusion was greater at the lower current density with correspondingly lower voltage and longer time.

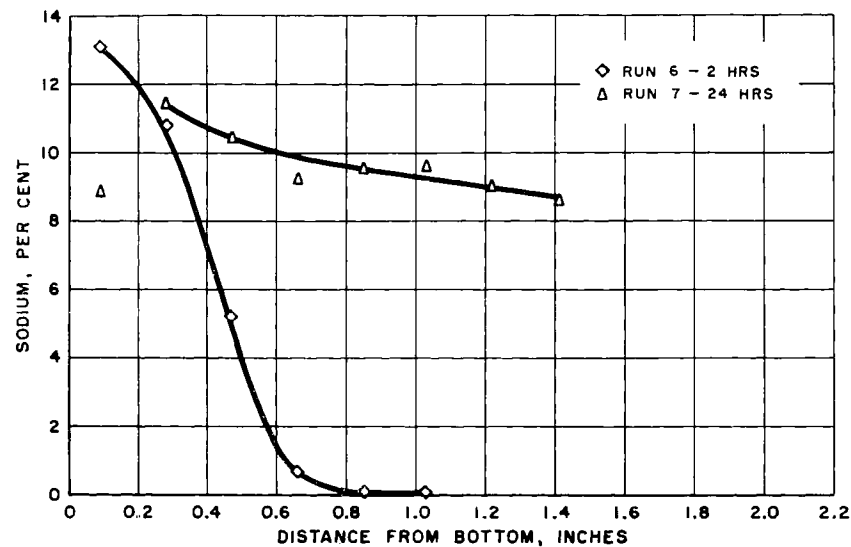


Fig. 3. Effect of time on diffusion of sodium from bath into carbon.

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In run 13 an electrolysis was carried out with two carbon specimens underneath a 2-in. aluminum pad. A carbon carrying no current was in the center of the crucible; the other, the cathode, was displaced 1/2 in. and directly under a suspended graphite anode. Diffusion (Table III) was comparable in both specimens. Thus, diffusion was not dependent on passage of current through the sample.

Run 14 demonstrated again that electrolysis was unnecessary for bath diffusion into carbon. A 1-in. cylinder of carbon was held below 2 in. of aluminum under molten bath with no current flowing for 6 hr at 970°C,

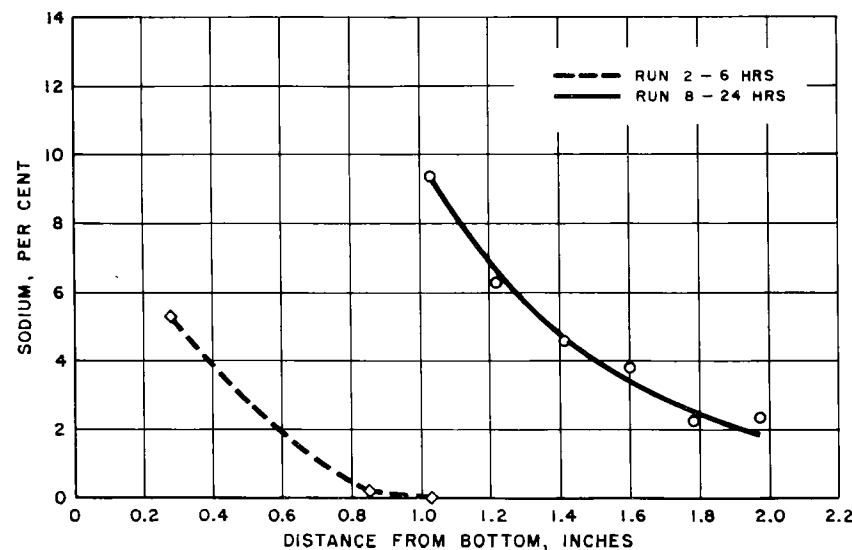


Fig. 4. Effect of time on diffusion into carbon under 2 in. metal pad.

but with a slow propeller-type stirrer extending through the bath into the metal pad. Diffusion (Table III) was equivalent to that of run 13 (Table III) with the conducting cathode, and somewhat greater than through the quiescent nonconducting cathode.

That sodium was a primary product in Hall bath electrolysis,<sup>3,4</sup> was shown by the initial wave of free sodium in carbon (Table IV) and by the dependence of sodium diffusion on current density (Table V). High current density implies a high rate of sodium generation. Furthermore, if sodium were a secondary product, its concentration in the bath would depend on bath composition. No evidence was found for this in runs where the bath composition was radically changed.

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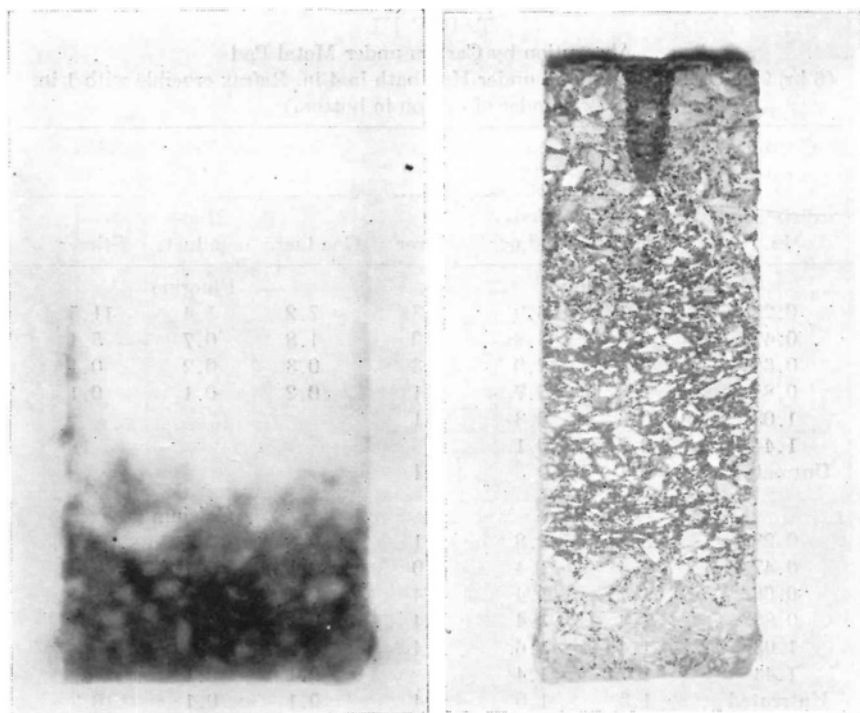


Fig. 5. Penetration of radioactive sodium. Left, autoradiogram. Right, photograph.

To determine the step following sodium absorption, a specimen impregnated at 445°C with 1.6% sodium was dipped 1/16 in. into Hall bath for 6 hr at 970°C with no current. Fluorine was absorbed corresponding to the formation of sodium fluoride. There was no increase in sodium content. Fluorine could have been transported as AlF or HF. The vapor pressure of AlF over Hall bath at 1000°C is 0.4 mm Hg.<sup>5</sup> The HF could be formed by hydrolysis. The vapor pressure of AlF<sub>3</sub> is negligibly low over Hall bath. If sodium tetrafluoroaluminate<sup>6</sup> were the transporting species there should have been a detectable increase in sodium content.

**Effect of Bath Vapors on Carbon**

Absorbed alkali metals<sup>7,8</sup> and other substances<sup>9-12</sup> spread the planes of graphite like an accordion and increase the interplanar spacing and crystallite height measured by x-ray diffraction. Experiments were run to determine whether vapors in an aluminum reaction cell<sup>3,13</sup> had a

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TABLE III

Absorption by Carbon under Metal Pad  
(6 hr, 970°C, 2 in. metal pad under Hall bath in 4 in. Refrax crucible with 1 in. cylinder of carbon in bottom)

Current run	Yes	Yes	No	Yes	Yes	No
	13	13	14	13	13	14
distance, in.	Non-Conduct.			Non-Conduct.		
	Conduct.	conduct.	Stirrer	Conduct.	conduct.	Stirrer
	Sodium			Fluorine		
0.28	8.1	6.9	9.3	7.2	5.4	11.5
0.47	6.0	3.8	7.2	1.8	0.7	5.1
0.66	3.1	2.0	3.3	0.3	0.2	0.1
0.85	1.8	0.7	2.1	0.2	0.1	0.1
1.03	0.6	0.3	0.1			
1.44	0.2	0.1				
Untreated	0.1	0	0.1			
	Aluminum			Calcium		
0.28	3.5	2.8	5.1	0.8	0.5	1.5
0.47	2.4	1.4	3.0	0.5	0.1	0.6
0.66	1.4	1.4	1.4	0.1	0.1	0.1
0.85	1.4	1.4	1.4	0.1	0.1	0.1
1.03	1.4	1.6	1.4	0.1	0.1	
1.44	1.7	1.4		0.1	0.1	
Untreated	1.3	1.0	1.4	0.1	0.1	0.2

TABLE IV

Diffusion of Bath Constituents into Carbon, Atom-%

		Distance, in.					
		0.28	0.47	0.66	0.85	1.03	1.22
Run 1	Na	43.4	49.6	57.6	57.1	29	98.7
6 hr	F	44.6	41.9	37.9	38.2	71	1.4
5 amp/in. <sup>2</sup>	Al	9.5	5.4	1.8	1.7		
1.50, 967°C	Ca	2.5	3.2	2.8	2.9		
Run 5	Na	43.5	69.3	94	92	100	
6 hrs	F	42.4	26.5	5	8		
5 amp/in. <sup>2</sup>	Al	10.8	2				
1.10, 971°C	Ca	3.3	2.4				
Run 3	Na	61.6	91.7	94.6			
6 hr	F	31.5	8.4	5.4			
1 amp/in. <sup>2</sup>	Al	4.1					
1.50, 969°C	Ca	2.8					

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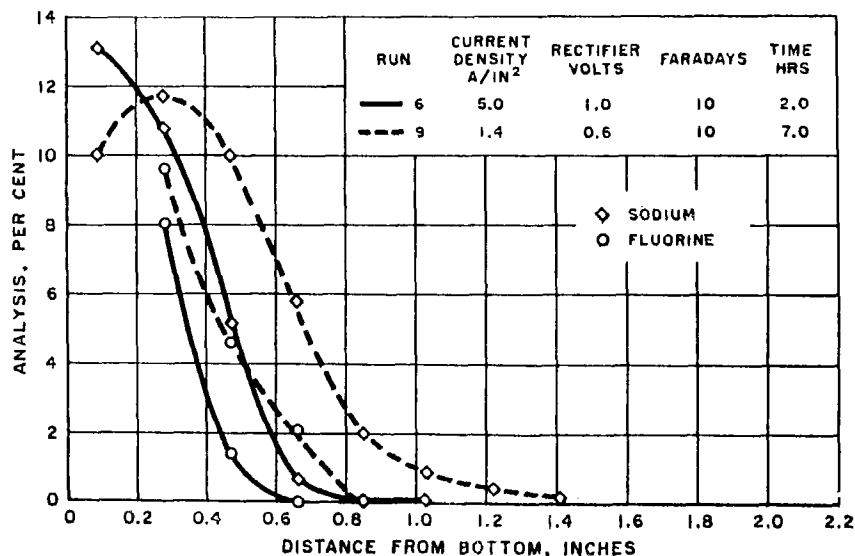


Fig. 6. Diffusion at constant faradays and different current densities.

similar effect on newly baked carbon whose crystallite height  $L_c^{15}$  is only 20 Å compared to over 300 Å for artificial graphites baked above 2500°C.

**Procedure**

Carbon specimens 1/2 by 1 in. in diameter were exposed in evacuated retorts made by welding shut 4 in. lengths of 2 in. diam heavy-wall steel pipe. The substance generating vapor for the test was at the bottom of the retort, and the carbon was suspended in the vapor by a molybdenum wire. After exposure at the appropriate temperature the retort was cut open. Specimens were measured and analyzed for absorption of vapors. Aluminum monofluoride was prepared by placing in the retort the

TABLE V  
Effect of Current Density on Diffusion into Carbon Cathode  
(All runs at 1.50 ratio, 970°C)

Run	Current density, amp/in. <sup>2</sup>	Na at 0.28 in., %
3	1	9.0
1	5	13.9
4	15	19.4

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stoichiometric amounts of aluminum and aluminum trifluoride, sodium tetrafluoroaluminate from the appropriate amounts of cryolite and aluminum trifluoride.

**Results**

Of the vapors that might exist over an aluminum reduction cell, only the alkali metals and calcium reacted with carbon (Table VI). Sodium attacked least, followed by lithium and potassium. Lithium and calcium formed carbides.

TABLE VI  
Effect of Vapors on Carbon Exposed for 17 Hours

Vapor	Temp., °C	Increase, %		
		Height	Diam	Weight
AlF	850	0	0	-0.07
Al	850	0	0	-0.47
NaAlF <sub>4</sub>	850	0	0	-1.24
Ca	850	1.5	2.1	17.6
Na	850	6.6	5.9	—
Li	850	—	Swelled completely	—
K	850	—	Swelled crumbled	—
AlF	950	0	0	—
Al	950	0	0	-0.1
NaAlF <sub>4</sub>	950	0	0	—
Na	950	6.1	4.4	6.3
Li	950	—	Viscous paste	—

Sodium absorption by carbon exposed under these conditions for 17 hr (Table VII) began at 550°C, reached a maximum in the 700–800°C range, and declined slightly at 950°C. With increasing exposure (Table VIII) absorption and expansion by the specimen greatly increased.

A cylinder of carbon, 3 in. in diameter, fitted with current and potential leads, was exposed to sodium vapor in an evacuated retort heated at 300°C per hour. Resistivity of the specimen remained constant to 650°C. At 710°C the resistivity had increased, and at 830°C it was comparatively high. This increase in electrical resistivity could be accounted for by expansion of the carbon and formation of minute cracks in the structure.

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Absorption by carbon of sodium at 850°C was greater from the liquid compared with the vapor. This can be explained in terms of equilibrium being reached much more rapidly with liquid sodium. With calcium the carbide was formed, and again more was formed with liquid calcium. Carbon lining did not react with aluminum at 850°C in 17 hr in these experiments.

TABLE VII  
Effect of Temperature on Absorption of Sodium by Carbon  
(All runs in evacuated retort for 17 hr)

Temp., °C	Increase, %			Na, %
	Height	Diam	Wt	
300	0	0	0.09	
400	0	0	0.09	
500	0	0	— 0.11	
550	0.8	0.6	2.7	
600	1.5	1.3	9.1	5.4
650	7.4	5	18.3	13.4
700	11	8.1	40.3	25
750	8.8	—	—	14.5
800	12.5	14.5	44.1	27
800	9.1	6.7	24.4	16.3
850	7.8	6.8	24.3	15.5
900	6.3	9.2	25.4	12.2
950	6.9	5.7	23.7	13

TABLE VIII  
Effect of Time of Exposure on Absorption of Sodium at 550°C

Time, hr	Increase, %			Na, %
	Height	Diam	Wt	
17	0.8	0.6	2.7	—
96	8.3	5.8	31.9	21.5
216	11.4	11.6	51.6	38.5

Graphite (types AGR and AGX) did not change dimensions on exposure at 850°C to aluminum or sodium tetrafluoroaluminate vapors for 17 hr, or to sodium at 950°C for 672 hr. It lost weight slightly in the presence of sodium, possibly as gaseous sodium carbide,  $\text{Na}_2\text{C}_2$ , which may be stable<sup>14</sup> between 900 and 1000°C.

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## Graphitization of Cell Lining

Carbon lining from old smelting cells was found to be highly graphitic by examination of the 002 band<sup>15</sup> obtained by x-ray diffraction of samples extracted with hot aluminum chloride solution and hydrochloric acid to remove the mineral matter (Table IX). For natural graphite the dis-

TABLE IX  
Degree of Graphitization of Carbon and Anthracite

Time in cell, days	$L_c, \text{Å}$	$d, \text{Å}$
None	20	3.521
None	18	3.477
1	26	3.523
1	35	3.463
88	176	3.397
140	284	3.377
170	266	3.381
306	380	3.377
828	346	3.383
1214	300	3.377
1216	255	3.383
1247	246	3.389
1270	222	3.386
1809	381	3.384
?	320	3.393
?	392	3.383
Anthracite, 2500°C <sup>a</sup>	260	3.368
Na at 950°C, 17 hr	20	3.50

\* See ref. 16.

tance between the graphite planes has a value of 3.35 Å, and the crystallite height  $L_c$  is very large. Graphitization of lining was equivalent to that of anthracite heated to 2500°C.<sup>16</sup> It did not correlate too well with age. To test the theory that a chemical mechanism such as decomposition of carbide<sup>17</sup> may have been responsible for the presence of graphitic carbon, a sample of carbon was exposed to sodium vapor at 950°C for 17 hr. Increased graphitization was not found, indicating the sodium carbide mechanism did not cause graphitization. Simple heating of anthracite with cryolite or alumina did not change the degree of graphitization.

## Mechanism of Carbon Deterioration in Reduction Cells

Considerable cracking may occur during baking of large monolithic carbon linings. After electrolysis begins, sodium released at the bath-

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metal pad interface, or formed by the reaction of aluminum with bath, dissolves in the metal pad and diffuses into the lining. At the same time the lining slowly graphitizes by a mechanism that was not established. A fluorine-containing species diffuses from the bath into the lining at a slower rate than the sodium. This slower rate may be attributed to the greater size of the molecule or lower vapor pressure. There it reacts with sodium, forming sodium fluoride and other products. This may be followed by diffusion of bath into pores containing sodium and sodium fluoride. While this diffusion might be as a liquid in experiments where the cathode was immersed from above (liquid sodium-sodium fluoride solutions exist at 960°C<sup>18</sup>), in a smelting cell where carbon lining is under the metal pad, vapor diffusion seems more likely.

Absorption of free sodium metal expands the lining. Expansions of this type have been found for other carbon systems.<sup>19</sup>

Because a reduction cell is enclosed by a steel shell, the expanded carbon lining buckles. This buckling is accompanied by formation and growth of cracks. These cracks fill with molten aluminum, which can eventually reach either the sides or steel collector bars and cause failure. Cracks formed during baking could be penetrated by liquid bath prior to formation of the metal pad.

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## Discussion

**E. A. Hollingshead** (*Aluminium Labs. Ltd., Arvida, Quebec*): A mechanism differing somewhat from that of the author is proposed for the absorption of sodium and fluorides by cathodic carbon, as follows:

1. Metallic sodium forms a solid solution in carbon and diffuses through the carbon lattice, rather than as vapor through the pores.

2. Penetration of molten electrolyte into the pores follows the diffusion of sodium because the wetting angle of electrolyte on carbon is decreased by sodium.

3. The reaction  $4\text{Na}_3\text{AlF}_6 + 3\text{C} + 12\text{Na} = \text{Al}_4\text{C}_3 + 24\text{NaF}$ , which is thermodynamically favorable, then occurs on the pore surfaces removing sodium from the carbon lattice and allowing more sodium to diffuse in.

It is believed that this mechanism is consistent with most of the author's results. His comments would be appreciated.

**M. B. Dell**: 1. Since the metal pad is at a temperature above the boiling point of sodium (883°C), initial movement of sodium to the carbon must be in the vapor phase, after which it diffuses through the carbon lattice or from crystallite to crystallite. It is not known whether sodium forms a solid solution in carbon or forms structures analogous to the alkali metal-graphite intercalates (A. Herold, *Bull. Soc. Chim. France*, **1955**, 999).

2. Reduction of wetting angle is a possible explanation.

3. This reaction as well as that between  $\text{NaAlF}_4$ , C, and Na is thermodynamically possible. We did not find  $\text{Al}_4\text{C}_3$  in short-term experiments, however.

**C. E. Pitt** (*National Carbon Co., New York*): The Russians state that swelling occurs only when current is applied. Please comment.

**M. B. Dell**: In their experiments the bath was not stirred. It is likely that rate of absorption is limited by the rate at which sodium is transported to the carbon surface.

**N. E. Richards** (*Reynolds Metals Co., Sheffield, Ala.*): Did you find any differences in carbon temperatures down into the lining?

**M. B. Dell**: Carbon temperature in the electrolysis experiments did not differ by more than 2° from bath temperature at a point 1.2 in. above the bath.

**H. Skantzé** (*Swedish Aluminium Komp, Stockholm, Sweden*): Have you investigated the effect of Cl?

**M. B. Dell**: No.

**O. Sandberg** (*Elektrokemisk, Kristiansand S, Norway*): What effect would you expect lithium fluoride to have on lining expansion?

**M. B. Dell**: The presence of lithium fluoride in the molten bath should cause greater swelling of carbon linings.