FORMATION AND DISTRIBUTION OF CYANIDE

IN THE LINING OF ALUMINUM REDUCTION CELLS

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The cyanide content of spent potlining spans four orders of magnitude in a single smelting cell. Typically over 90% of the cyanide is found in the ends and sides of the cells; little is found in the cathode blocks and bottom insulation. Nearly 80% of the cyanide can be extracted by a water leach and most of that is amenable to chlorination. Cyanide is found in non-carbonaceous materials indicating it forms elsewhere and migrates to relatively cool regions of the cells.

Conditions within a smelting cell favor formation of NaCN. Bench scale experiments show nitrogen$_{(g)}$ reacts readily with sodium impregnated carbonaceous materials at 800°C to form substantial quantities of NaCN in short exposure periods. Graphite and semi-graphite impregnated with Na yield several fold more NaCN in short term tests under nitrogen$_{(g)}$ at 800°C than do anthracite carbon block specimens. The likely source of the nitrogen is air inleakage rather than nitrogen in the lining materials.

Introduction

The lining material in an aluminum reduction cell must be replaced periodically. Typical lining life is three to seven years. The spent potlining (SPL) presents a unique high volume disposal problem due to its fluoride and cyanide content.

Spent potlining has long been regarded as a valuable resource and recycled to some degree. There are extensive efforts in progress today to expand SPL recycling (1), but a recycling process applicable to the industry in general is still out of reach. Furthermore, few of the recycling options under study can readily accept the entire potlining.

This study was undertaken to

1.   Characterize SPL to determine if segregation of the fractions would facilitate recycling and/or reduce the amount of potentially hazardous material, and

2.   Gain fundamental information about cyanide formation to determine if it would be practical to limit its formation.

Field Sampling

Experimental Procedure

Extensive sampling was done to establish the amount and distribution of fluoride and cyanide in typical linings. Samples were taken from seven cells ranging in size from a nominal 65 Kamp to 225 Kamp. Some of the cells had been wetted with water to facilitate digging while others were not. To provide access to the sampling areas, one quadrant of each cell was removed by digging vertically down to the bottom of the steel shell. From these exposed faces, at the centers and ends of the cells, about fifty 500 g samples were removed with the aid of pneumatic and hand tools. Each sample was from a predetermined grid location designed to include each constituent of the cell lining.

The sample handling procedures conformed with those described in SW846 (2). All material was placed in light blocking, polyethylene bottles immediately after removal from the smelting cell. The bottles were held at ice temperatures and transported to Alcoa's R&D center. There each sample was crushed to -9.5 mm, riffled, and two 50 gram samples were removed and ground to -60 mesh. The samples continued to be refrigerated until analyzed.

Total fluoride and water soluble fluoride were determined using standard Alcoa procedures. The total fluoride determination was made by fluoride specific ion electrode, SIE, after ashing and fusing. The soluble fluoride was determined by SIE after a hot water leach of the ground material. The hot water leach procedure utilized 1 g solid in 250 ml water at 80°C for 30 min.

Total cyanide and weak acid dissociable cyanide were determined on the solid using standard ASTM procedures. ASTM D2036-80 Method A was used to determine the total cyanide. ASTM D2036-80 Method C was used to determine weak acid dissociable cyanide. Total water soluble cyanide and amenable leachable cyanide were determined by EPA Method 335.3 and ASTM D2036-80 Method C, respectively. The leaching procedure consisted of placing one-half gram -60 mesh material in 500 ml DI water for 1 hour then filtering through a .45 micron filter.
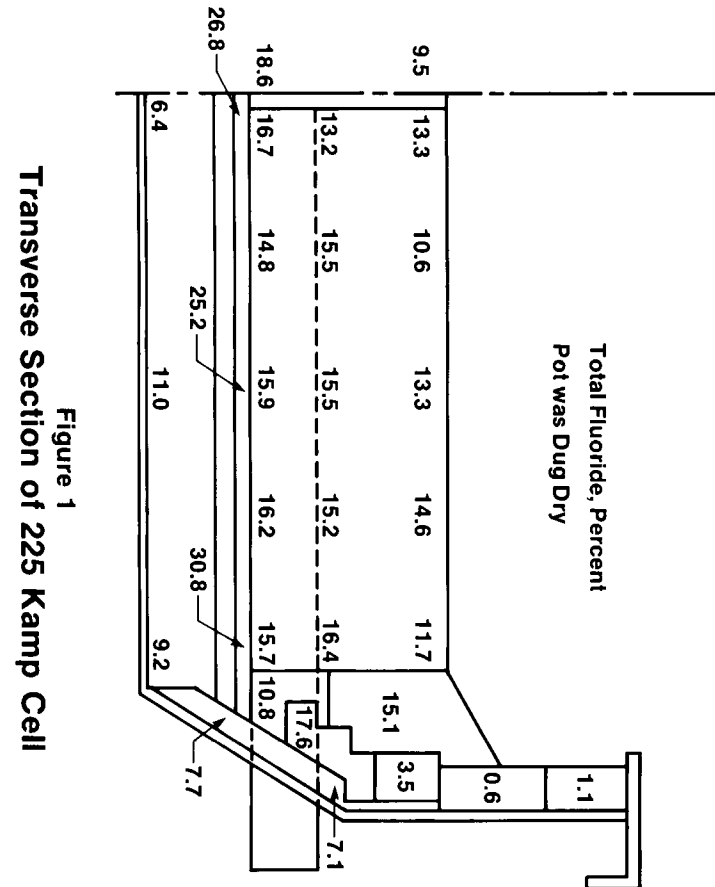
Results and Discussion

Distribution of fluoride in a 225 Kamp cell is shown in Figures 1 and 2. The values were fairly uniform for the interior of the cell. Near the ends and sides of the cell the concentrations were lower because of the lower temperatures there. The insulation under the cathode blocks had absorbed appreciable fluoride during the 2400 days of operation.

Relative cyanide concentrations for this same cell are shown in Figures 3 and 4. The cyanide values at the interior of the cell were low while higher concentrations were found at the ends and sides. The insulation under the cathode blocks contained little cyanide.

A summary of results from sampling other cells is shown in Table I. The pattern was similar for smaller cells dug either wet or dry -- the interiors had the lowest concentrations and the ends and sides were higher. Over 90% of the total cyanide was found in the ends and sides of the cells.

TABLE I

Summary of Cyanide Sampling Results

Sample	Pot Size (Kamp)	Pot Age (days)	Digging Practices	Side Walls	End Walls	Cathode Blocks	Bottom Insulation
				Cyanide Content, Weighted avg., percent of total			
1	225	2400	Dry	30	67	1	2
2	225	2400	Wet	35	64	1	1
3	225	800	Wet	50	45	2	3
4	90	1800	Dry	20	75	2	3
5	90	1100	Wet	44	52	2	2
6	65	900	Dry	8	72	19	1
7	65	1100	Wet	11	80	8	1
Avg.	--	--	--	28	65	2	2

Figure 1
Transverse Section of 225 Kamp Cell

Total Fluoride, Percent
Pot was Dug Dry

**Total Fluoride, Percent
Pot was Dug Dry**

11.0 12.5 11.7
10.2
15.6 12.8

11.0 12.4
14.0
13.2 15.6
17.1

26.4 19.6
4.8
2.1
15.0
5.2

27.3 29.3 15.6 8.7 30.4 12.8 4.4 21.6

**Figure 2
Longitudinal Section of 225 Kamp Cell**

**Dry Dug
Relative CN⁻ Concentration**

VL VL VL
VL
VL VL VL
VL VL
VL
VL
L
M
L M
H H
H H H M
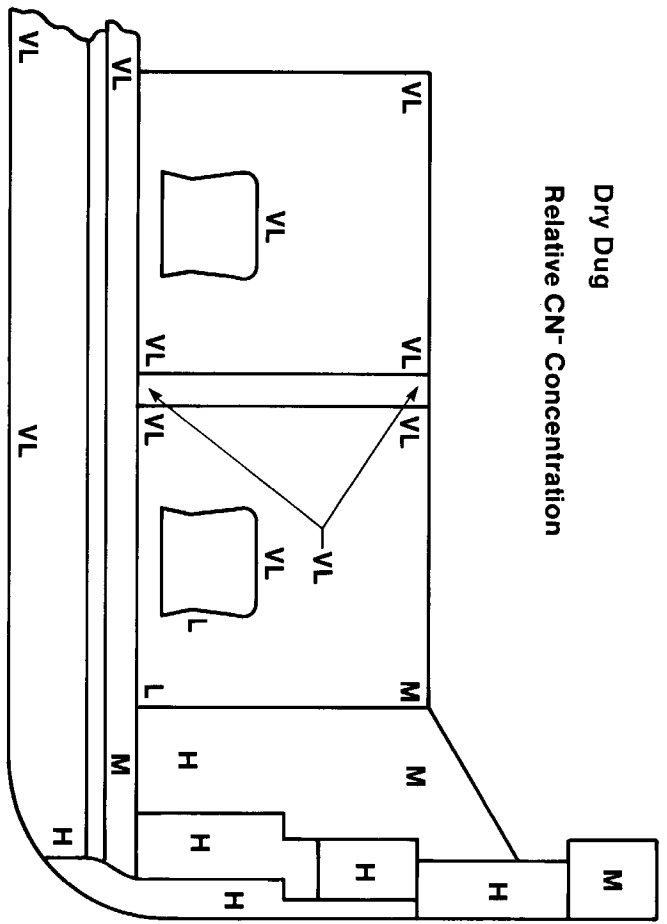
**Figure 3
Longitudinal Cross Section of 225 Kamp Cell**

Some typical analyses of the forms of cyanide and fluoride in potlining are tabulated in Table II. The first 15 lines represent individual small samples of SPL. The last 2 lines represent composite samples of SPL from two different reduction cells. The extreme variability between the individual samples points out the need to use composite samples when making basic conclusions relative to the composition of SPL.

Noteworthy observations from the data in Table II are:

1. A large amount of the cyanide in SPL is water soluble -- approximately 75-80%.

2. Approximately 75% of the water soluble cyanide is amenable to chlorination.

3. Approximately 40% of the total fluoride in SPL is water soluble in hot water.

TABLE II

Form of Cyanide and Fluoride in SPL

| | Water Soluble CN | | Water Soluble F |
	(% of total)	Amenable[1] (% of total)	(% of total)
1	88	84	85
2	72	72	27
3	100	57	87
4	67	13	27
5	90	51	65
6	48	32	23
7	41	19	72
8	82	82	18
9	100	80	91
10	10	3	17
11	94	94	99
12	93	37	41
13	55	34	15
14	100	85	90
15	82	82	18
Avg., Std. Dev.	75±26	55±30	50±34
Composite 1	79	--	37
Composite 2	82	--	38

[1]·Amenable to chlorination

Dry Dug
Relative CN⁻ Concentration

Figure 4
Transverse Section of 225 Kamp Cell

The mechanism of formation of the sodium cyanide could not be unequivocably stated from these sampling results. Sodium and carbon are found in plentiful amounts in cell linings. The source of nitrogen is less clear. Nitrogen from the air and heterogenous nitrogen in the carbon lining are two possible sources. To help judge the relative importance of these two, bench scale tests were run. A literature search of commercial processes aided in designing the experiments.

Laboratory Experiments

Experimental Procedure

The bench scale experiments to form cyanide were carried out in a reactor made of 38 mm (1.5 in.) diameter Type 304 stainless steel, 711 mm (28 in.) long. The ends were capped with Swagelok fittings. The purge gas was kept at 22.4 torr (12 in. of H_2O) above atmospheric pressure. The reactor was heated by a horizontal tube furnace with 457 mm (18 in.) heating elements, controlled by a thermocouple in the center of the reaction tube. A thermocouple mounted between the outside of the reactor and the furnace element provided a signal for over-temperature control.

The carbon samples were machined half-cylinders with a slot cut in the flat side to hold the sodium source (sodium metal or sodium carbonate). The carbon samples all weighed between 20 and 30 grams.

The reagents were placed in the top slot on the carbon sample and the complete system was inserted into the reactor. The reactor was purged with the gas to be used for the experiment (argon or nitrogen) at room temperature. The total purge amounted to over 18 times the reactor volume. The purge was continued at a lower rate while the reactor was heated to the temperature of the experiment. The flow was shut off once the system reached the experimental temperature, but the reactor was kept at a purge gas pressure 14.9 torr (8 in. of H_2O) above atmospheric pressure for the balance of the experiment.

The system was allowed to cool to room temperature. The sample was removed from the reactor and sealed in an opaque plastic sample bottle. The reactor was washed with 20 g/L NaOH to remove any remaining salts. Carbon samples were analyzed for total cyanide and soluble cyanide.

Results and Discussion

Results of the experiments performed are shown in Figures 5-8. The reaction of sodium, carbon, and elemental nitrogen produced cyanide more rapidly than any other route (Figure 5). The carbons which were more graphitic produced more cyanide (Figure 7).

Sodium carbonate was much less effective for cyanide production than sodium metal (Figure 8). It is commonly found where the collector bars exit the shell. This result agrees with the literature on commercial cyanide production. (3,4)
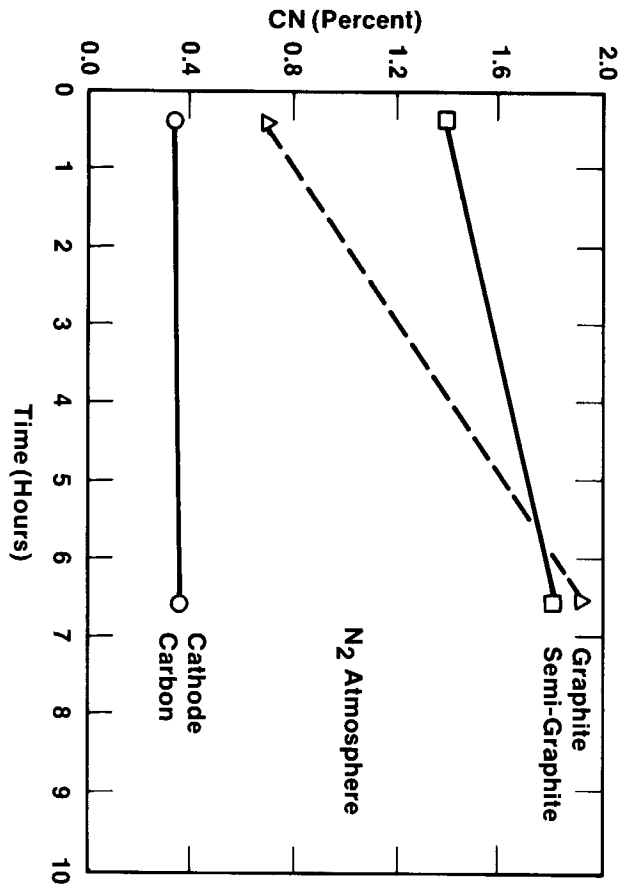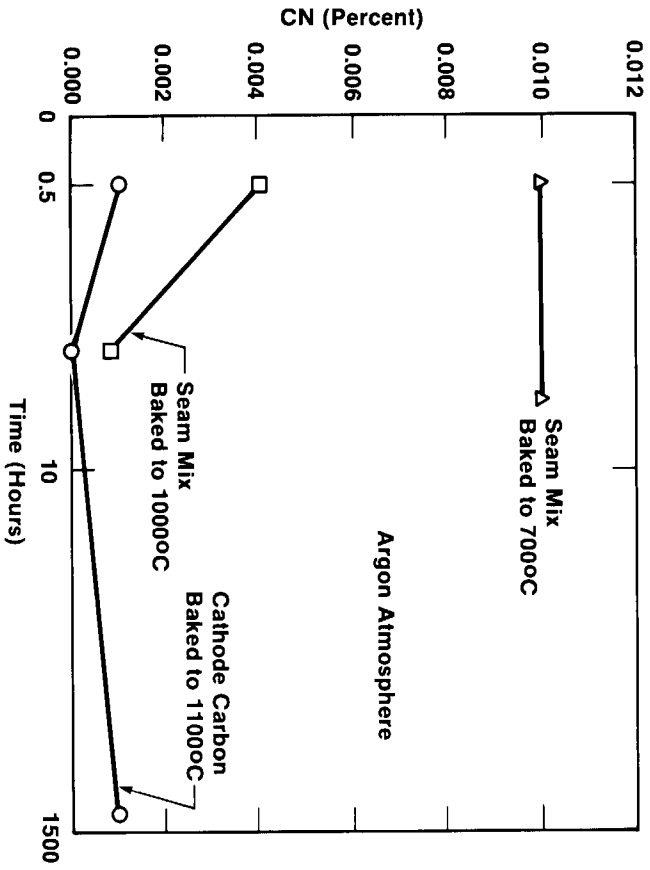

Figure 5
Effect of Nitrogen Source

Figure 6
Effect of Carbon Baking Temperature
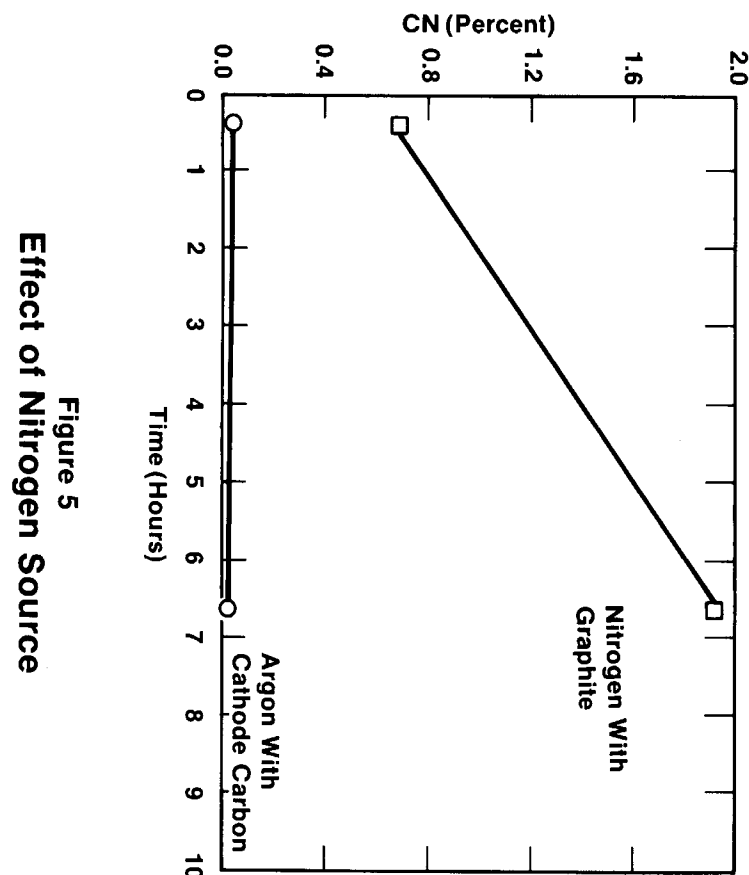
Figure 7
Effect of Carbon Type

The chemically bound nitrogen in the carbon was much less effective for cyanide production than elemental nitrogen (Figure 5). Seam mix baked at 700°C provided the most cyanide, probably due to the aromatic nitrogen compounds in the pitches used (Figure 6). The nitrogen in the electrically calcined anthracite (the major component in cathode carbon) may also be present as stable nitrides (AlN, Si_3N_4)(5) which cannot be converted to sodium cyanide. The cyanide levels in these cases generally decreased with increasing exposure time (Figure 6). This is consistent with the observed thermal decomposition of sodium cyanide at temperatures above 600°C. (3) Nitrogen determinations in carbon at low levels (<0.75 wt%) were inconsistent with literature values and depended on the apparatus used.

One test was run for 62 days in order to test formation of cyanide from bound nitrogen in cathode carbon. This time comes closer to the usual operating life of a Hall cell than the other tests in this work. Vapor transport of sodium was expected during this lengthy test, and white deposits observed in the reactor tube are evidence that it did occur. It was also expected that cyanide would decompose, releasing sodium and elemental nitrogen. This must have occurred since this test produced no detectable cyanide (compared with some cyanide in shorter tests of the same system). Thus it can be postulated that cyanide formation depends on the continued sodium production found in normal Hall cell operation.

Considering all of this information, it seems likely that much of the NaCN found in cell linings forms at the ends and sides of the cells where carbon is in contact with air and sodium permeates the lining early in the life of the cell. The resultant NaCN then diffuses deeper into the lining. It is found in insulating material which originally had none of the requisite elements.

It is possible that air inleakage around the collector bars plays a part but the evidence here does not support this. Heterocyclic nitrogen in the anthracite or binder may also be a source but not the primary one. Other possible sources such as nitrogen dissolved in the bath are a matter of conjecture at this time.

Conclusions

1. The cyanide content of SPL was found to span four orders of magnitude in a single smelting cell.

2. Total fluoride content of SPL ranged from <1% to 36%; it was generally in the range of 10-15%.

3. Highest cyanide concentrations were found in the ends and sides of the cells. The end and side lining typically contained over 90% of the cyanide in a spent cell. Selective removal of SPL would greatly reduce the volume of cyanide bearing waste.

4. High concentrations of cyanide were found in some of the non-carbonaceous materials indicating that it formed elsewhere and migrated to the cool regions of the cell.

Figure 8
Effect of Na2CO3
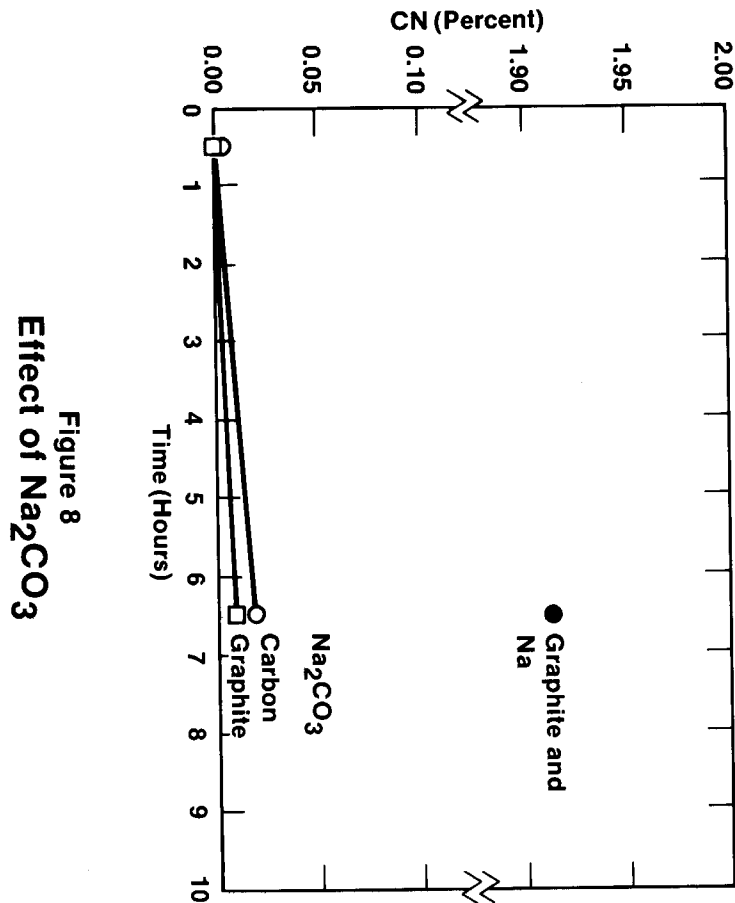
5. Nitrogen was found to react readily with sodium impregnated carbonaceous materials at 800°C to form substantial quantities of NaCN in short exposure periods.

6. Air inleakage rather than nitrogen in the lining materials was considered the likely source of the nitrogen needed to form cyanide. As it would be difficult to stop air inleakage, it would appear difficult to limit the formation of cyanide.

7. The method of digging, wet vs. dry, had little impact on the amount or distribution of cyanide.

8. A large portion (80%) of the total cyanide present in composite samples of SPL was soluble in water. A high percentage of this water soluble cyanide was amenable to chlorination. Approximately 40% of the total fluoride was water soluble.

References

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