Essential Readings in Light Metals: Electrode Technology for Aluminum Production.
Edited by Alan Tomsett and John Johnson.
© 2013 The Minerals, Metals & Materials Society. Published 2013 by John Wiley & Sons, Inc.

THERMAL TREATMENT OF SPENT POTLINER IN A ROTARY KILN

Dennis G. Brooks, Euel R. Cutshall
Reynolds Metals Company
Manufacturing Technology Laboratory
3326 East Second Street
Muscle Shoals, AL 35661-1258

Donald B. Banker
Reynolds Metals Company
Hurricane Creek Plant
P. O. Box 97
Bauxite, AR 72011

Dennis F. Strahan
Reynolds Metals Company
Primary Metals Division
P. O. Box 27003
Richmond, VA 23261-7003

A process has been developed for detoxifying spent potliner (SPL) in which the SPL is blended with limestone and an anti-agglomeration agent and thermally treated in a rotary kiln. The process is very effective for destroying cyanides and significantly reduces the concentration of soluble fluorides in the kiln residue. The process uses a relatively simple, proven technology that is economically competitive to landfilling. Over 300,000 tons of SPL from several sources within Reynolds Metals Company has been treated successfully. The EPA has proposed to grant Reynolds' petition to exclude up to 300,000 yd^3 per year of kiln discharge from the list of hazardous wastes conditional upon the discharge meeting certain criteria.

Introduction

In the process of aluminum production, alumina is dissolved in molten cryolite in electrolytic cells, or pots, where the alumina is electrolytically reduced to aluminum metal. A number of pots, usually more than 100, are arranged in series to form a potline; an aluminum production plant may have several potlines. The pots contain a molten electrolyte consisting primarily of cryolite (Na_3AlF_6) and operate at approximately 930 to 1000°C. Other materials are added to the electrolyte to improve the efficiency of the operation or to reduce power consumption: Alumina, aluminum fluoride, sodium fluoride, soda ash, calcium fluoride, lithium carbonate and magnesium oxide.

The hearth or lining of the cell is composed of carbon, which is backed by insulation and contained within a steel container called a potshell. The carbon portion of the lining serves as the cathode and contains the molten electrolyte. The carbon lining is composed of prefabricated carbon blocks joined together by a carbon paste, which is hydraulically rammed in the seams between the carbon blocks. The sidewalls of the lining are also typically formed with carbon paste, but may contain prefabricated carbon blocks. The carbon material within the lining, both blocks and paste, are predominantly anthracite-based materials. They may contain some graphite to improve their electrical and thermal properties. Insulation packages for a cell are mostly of two types -- a bed of alumina, or refractory brick and/or castable.

Over the life of the cathode (cell lining), the carbon and insulating materials become impregnated with fluoride-containing salts. As the ingress of salts continues, the integrity of the lining is adversely affected. Sodium, in particular, can actually intercalate within the crystalline lattice of the carbon materials, causing distortion and stresses within the lining. The insulating materials become more thermally conductive as they are impregnated by these fluoride salts. Failure can occur by cracking or excessive heaving of the lining. When these failures occur, the cell is taken off-line and the cathode lining material is removed from the potshell by mechanized digging equipment. Once this cathode lining is removed from the shell it is referred to as spent potliner (SPL). The life cycle of a cathode can be from three to ten years. Since there are numerous pots located at a single aluminum reduction plant, the decommissioning and relining of cathodes is a continual process.

In addition to containing fluoride salts as mentioned above, SPL contains cyanides that are formed by the ingress of air through openings in the potshell and the subsequent reaction of nitrogen with the carbon lining. Therefore, cyanide is concentrated around the perimeter of the cathode, predominantly in the rammed endwalls and sidewalls of the carbon lining. As the size, or capacity, of the cell is increased, the ratio of the mass around the cell periphery to the total mass of the cathode lining is reduced, and the composition of cyanide in the spent potliner is reduced accordingly. Therefore, the concentration of cyanides in older (smaller), more air-permeable cathodes is greater than in larger more modern cells.

Spent potliner contains a small amount of semi-volatile organics which, in all probability, originate from the carbon paste used to fill the seams between the cathode blocks and to form the cathode sidewalls and endwalls. The carbon paste forming the outermost part of the sidewalls (closest to the steel potshell) is not baked to sufficiently high temperatures during cell operation to carbonize all of the pitch used as a binder in the paste. A small portion of the semi-volatile organics then remain in the spent potlining. Again, the amount present can be related to the physical size of the cathode. The larger and thicker the sidewalls, the less likely that the outermost paste will be completely baked.

Spent potliner was listed by EPA on September 13, 1988 (53 *Fed. Reg.* 35412) as a hazardous waste (K088) under 40 C.F.R., Part 261, Subpart D because it may contain significant amounts of iron cyanide complexes and free cyanide. These recent actions create an immediate need in the aluminum industry for an economical process for detoxifying spent potliner such that the treated residue is not a hazardous waste. This is important because of the need for alternatives to land disposal of hazardous waste, established as national policy in the RCRA Hazardous and Solid Waste Amendments (HSWA) of 1984, and the anticipated lack of hazardous waste treatment capacity.

A review of the literature shows the composition of SPL to be highly variable. The range of analyses is given in Table I. Any process for the treatment of SPL must be versatile enough to treat SPL generated while using different cell designs, electrolyte compositions, and insulation packages; and any residues generated must meet anticipated EPA-defined limits for all constituents of concern (e.g., cyanide, fluoride, organics and metals). The components of SPL of greatest concern environmentally are cyanide and soluble fluoride salts.

Table I. Spent Potliner Constituents

	Range of Compositions, %
C	9.6-51.0
Na	7.0-20.0
Al	4.7-22.1
F	9.7-18.9
Ca	1.1-2.9
Li	0.3-1.1
Mg	0.3-0.9
Si	0.0-12.3
Fe	0.3-2.1
S	0.1-0.3
CN	0.02-0.44

The aluminum industry has long recognized the environmental challenges of SPL and is pursuing many options for treatment and/or disposal. These options include: Landfilling; recycle as a feedstock in other industries (such as the steel, cement, aluminum or mineral wool industries); fluidized bed combustion; cryolite recovery; pyrohydrolysis, pyrosulfolysis and others. Landfilling is an option that is presently available but will become increasingly expensive since hazardous waste landfills are required. Recycling through other industries is an attractive and proven option; however, the classification of SPL as a hazardous waste greatly discourages other industries from utilizing SPL due to the cumbersome and expensive environmental regulations. Some of the other technologies may eventually have application, but many involve excessive cost and have never been proven on an industrial scale.

This paper discusses still another process for SPL treatment and disposal - thermal treatment in a rotary kiln. The process has the advantage of using a relatively simple, proven technology that is also economically competitive to landfilling. The process was developed and utilized for more than two years on an industrial scale at Reynolds idled Hurricane Creek Alumina Plant in Bauxite, Arkansas. Over 300,000 tons of SPL was treated during this period.

Process Concept

The concept of the process is shown schematically in Figure 1. A blend of pre-sized SPL, limestone (LS) and anti-agglomeration additive (AA) is fed to the rotary kiln and thermally treated. The cyanides are destroyed by oxidation at elevated temperature and the soluble fluoride salts react with the limestone to form calcium fluoride, a stable and relatively insoluble form of fluoride. The AA is blended with the SPL and LS in an amount sufficient to prevent the agglomeration of the solids as they pass through the kiln. The kiln discharge contains very low levels of cyanide and soluble fluorides.

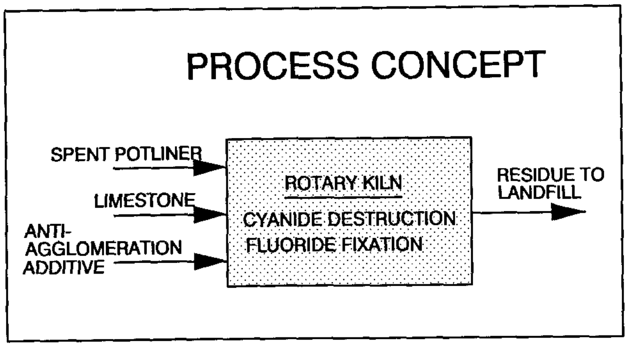

Figure 1. A blend of spent potliner, limestone and anti-agglomeration additive is thermally treated in a rotary kiln to destroy the cyanides and convert the soluble fluorides to an insoluble form.

Process Description

A schematic diagram of the process is shown in Figure 2 and a complete description follows.

Crushing, Sizing and Handling

The spent potliner was downsized using impact crushers and hammer mills. The generation of a large amount of very fine material is to be avoided as much as possible because of material handling concerns. The number of crushing and screening stages that are required is dependent on the desired maximum particle size which, in turn, is dependent upon the initial contents of cyanide and fluoride salts in the SPL.

The limestone may be crushed with the spent potliner in the crushing circuit, crushed separately or purchased pre-crushed. Iron and scrap aluminum must be removed from the SPL to prevent damage to the crushers.

All areas where SPL is handled (shipping, off-loading, conveying, storage, crushing, etc.) must be well ventilated. SPL will react with moisture and generate ammonia, methane and hydrogen which, if allowed to accumulate, can present an explosion hazard. Also, if water has been added, the SPL is difficult to crush and convey. For these reasons, every effort should be made to keep the SPL as dry as possible and in well ventilated areas.

Feed System

The feed system used was a series of conveyors, elevators and tanks as shown in Figure 2. The blend of SPL, LS and AA was controlled by varying the corresponding feed rates of each material to a common conveyor belt. The mixture was then transferred to the feed surge tank by a bucket elevator. A weigh belt feeder was used to control the rate at which the mixture discharges from the feed tank. From the feed tank several conveyors were used to transfer the material into the kiln.

Close control of the feed blend was essential to ensure an acceptable product and to avoid agglomeration within the kiln.

Rotary Kiln and Auxiliaries

The kiln used for treating SPL had been used in the past to calcine alumina trihydrate. It is approximately 250 feet long by 9 feet in inner diameter, and is refractory lined except for the first 70 feet at the feed end. Several refractory dams are located along the length of the kiln; however, a large 30-inch dam at the exit of the kiln was removed prior to start-up. Operation is in the counter-current mode in that the fuel (natural gas) and solids are introduced at opposite ends of the kiln and travel in opposite directions. The temperature of the product was measured using a thermocouple embedded in the solids as they were discharged from the kiln.

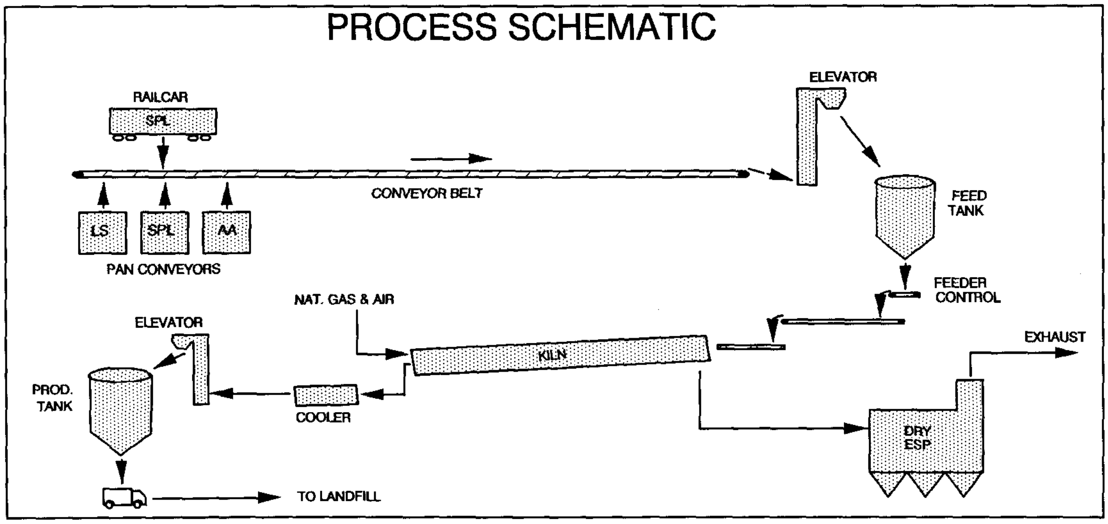

Figure 2. Schematic of the process for the thermal treatment of spent potliner in a rotary kiln. SPL = spent potliner; LS = limestone; AA = anti-agglomeration additive.

The solids, after discharge from the kiln, passed through a steel grating to remove large clinkers or loose bricks and then were directed into a rotary cooler. The cooler was of the shell and tube design with the solids passing through the tubes. Cooling air was drawn through the shell after which it was used as primary air in the kiln burner firing system. The solids were discharged from the cooler onto a bucket conveyor and were then transferred into a holding tank. From the holding tank, the material was loaded onto trucks and transferred to the landfill.

The exhaust gases from the kiln passed through a series of dust removal equipment including a large cyclone, a bank of small cyclones (multiclones) and finally a dry electrostatic precipitator (ESP).

A photograph of the alumina kilns and ESPs at the Hurricane Creek Plant is shown in Figure 3.

Operations

After securing the necessary environmental permits for operations and landfilling, the process was started in March 1988. Operations were discontinued on June 30, 1990, the effective date on which SPL became a listed hazardous waste in Arkansas. During this time over 300,000 tons of SPL were treated.

The operating parameters for the kiln are summarized in Table II.

Table II. Kiln Operating Parameters

Feed Rate	18-26 tph
Discharge Temperature	1100-1600°F
Firing Hood Vacuum	0.4-0.6" H_2O
ESP Temperature	350-400°F
Rotational Speed	1.25 RPM
Fuel Consumption	3.1-3.6 MM Btu/ton SPL

Results And Discussion

Spent Potliner

To demonstrate the capabilities of the thermal treatment process, results are presented for the processing of SPLs from two plants within Reynolds. SPL from Source No. 1 is from a small, low-capacity prebake reduction cell, whereas SPL from Source No. 2 is from a larger-capacity, Soderberg reduction cell.

The processing parameters were optimized for each source of SPL to achieve the desired level of detoxification. After the parameters were optimized and after the kiln had achieved steady-state operations, the SPL and kiln discharge (KD) were sampled at 15-minute intervals. The samples were collected over a six-hour period and composited into a single sample for analysis. Sampling continued over a 24-hour period resulting in 4 composite samples each of SPL and KD. This sampling was carried out for each source of SPL. The analytical results of the four composite samples of each SPL and KD were averaged. The average analyses for the untreated SPL and for the KD are given in Tables III and IV, respectively.

Table III. Analysis of Spent Potliner

Component	Units	SPL Source No. 1	SPL Source No. 2
Elemental Analysis	wt.%		
Carbon		24.75	16.89
Sodium		19.50	19.36
Aluminum		20.42	20.42
Fluorine		17.93	21.36
Calcium		2.26	2.00
Lithium		1.10	0.88
Magnesium		0.53	0.93
Iron		0.69	0.54
Silicon		0.79	0.03
Sulfur		0.20	0.23
Total Cyanide	mg/kg	2800	343
Total Metals	mg/kg		
Antimony		<3.3	9.8
Arsenic		<40	<20
Barium		164	140
Beryllium		17	31
Cadmium		<0.44	<0.44
Chromium		20	12
Cobalt		4.7	2.8
Copper		57	46
Lead		14.5	10
Mercury		<0.10	<0.10
Nickel		43.4	47
Selenium		<2.0	<4.0
Silver		<1.0	<0.69
Thallium		<0.50	<0.50
Tin		97	148
Vanadium		31	35
Zinc		25	39
Semi-Volatile Organics	mg/kg		
Anthracene		<10	<10
Benzo(a)anthracene		28	29
Benzo(a)pyrene		37	36
Benzo(b)fluoranthene		81	109
Benzo(k)fluoranthene		81	109
Benzo(g,h,i)perylene		21	26
Bis(2-ethylhexyl)phthalate		<10	<10
Chrysene		41	57
Dibenzo(a,h)anthracene		<10	<11
Di-n-octylphthalate		<10	<10
Fluoranthene		42	48
Indeno(1,2,3-cd)pyrene		22	21
Phenanthrene		25	<16
Pyrene		32	41
EP Toxicity	mg/l		
Cyanide		145	46
Fluoride		1456	925

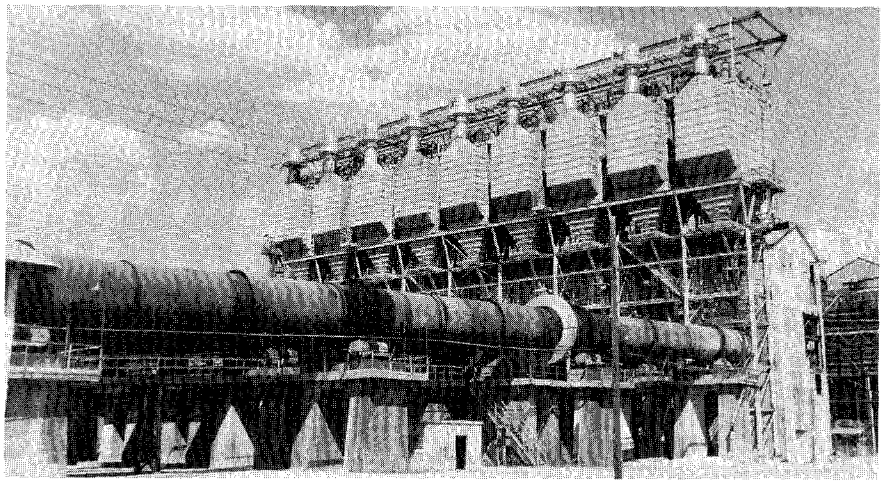

Figure 3. View of alumina calcining kilns and dry ESPs at Hurricane Creek. The kilns are 250' long by 9' I.D.

Table IV. Analysis of Kiln Discharge

Component	Units	SPL Source	
		No. 1	No. 2
Total Cyanide	mg/kg	12	<6.6
Total Metals	mg/kg		
Antimony		14	27
Arsenic		<40	<20
Barium		102	100
Beryllium		6.7	12
Cadmium		0.69	<0.40
Chromium		65	60
Cobalt		13	13
Copper		15	27
Lead		4.3	9.0
Mercury		<0.1	<0.1
Nickel		27	28
Selenium		<2.0	<4.0
Silver		3.2	2.2
Thallium		<0.5	<0.50
Tin		75	94
Vanadium		91	102
Zinc		26	32
Semi-Volatile Organics	mg/kg		
Anthracene		<1.0	<1.0
Benzo(a)anthracene		<1.0	<1.0
Benzo(a)pyrene		<1.0	<1.0
Benzo(b)fluoranthene		<1.0	<1.0
Benzo(k)fluoranthene		<1.0	<1.0
Benzo(g,h,i)perylene		<1.0	<1.0
Bis(2-ethylhexyl)phthalate		<1.0	<1.0
Chrysene		<1.0	<1.0
Dibenzo(a,h)anthracene		<1.0	<1.0
Di-n-octylphthalate		<1.0	<1.0
Fluoranthene		<1.0	<1.0
Indeno(1,2,3-cd)pyrene		<1.0	<1.0
Phenanthrene		<1.0	<1.0
Pyrene		<1.0	<1.0
EP Toxicity	mg/l		
Antimony		<0.20	<0.20
Arsenic		0.017	0.06
Barium		0.21	0.091
Beryllium		0.0034	<0.002
Cadmium		0.0053	<0.005
Chromium		<0.010	<0.03
Cobalt		<0.010	<0.01
Copper		<0.020	<0.02
Lead		0.0069	0.016
Mercury		<0.0002	<0.0002
Nickel		<0.02	<0.02
Selenium		0.0042	0.0034
Silver		0.01	<0.03
Thallium		<0.02	0.0082
Tin		<0.60	<0.6
Vanadium		0.038	0.044
Zinc		0.37	<0.02
Ammonia (as N)		3.5	1.8
Cyanide		0.12	<1.1
Fluoride		16	21
TCLP	μg/l		
Acenapthene		<0.910	NA
Benzo(a)anthracene		<0.036	NA
Benzo(a)pyrene		<0.012	NA
Benzo(b)fluoranthene		<0.022	NA
Chrysene		<0.075	NA
Fluoranthene		<0.235	NA
Indeno(1,2,3-cd)pyrene		<0.022	NA
Pyrene		<0.140	NA
Reactivity	mg/kg		
Cyanide		<0.25	<0.25
Sulfide		<30	<20
Oil and Grease	mg/kg	56	27

NA = not available.

Detoxification

A comparison of the analyses between SPL and the corresponding KD is shown in Table V regarding cyanide, fluoride and semi-volatile organics. As can be seen, the concentrations of these constituents are much less in the KD than in the original SPL. A portion of this reduction is due to dilution of the SPL with other solids (limestone and anti-agglomeration additive); however, the degree of detoxification is much greater than that accounted for by dilution alone. The efficiencies given in Table V have been corrected for the fraction of SPL in the kiln feed.

Table V. Detoxification of Spent Potliner By Thermal Treatment in a Rotary Kiln

Spent Potliner Source	1	2
Spent Potliner		
Total Cyanide, mg/kg	2800	343
Soluble Cyanide, mg/l	145	46
Soluble Fluoride, mg/l	1456	925
Semi-Volatile Organics, mg/kg[1]	<410	<533
Kiln Discharge		
Total Cyanide, mg/kg	12	<6.6
Soluble Cyanide, mg/l	0.12	<1.1
Soluble Fluoride, mg/l	16	21
Semi-Volatile Organics, mg/kg[1]	<14	<14
Detoxification Efficiency, %[2]		
Total Cyanide Destruction	98.6	>95.2
Soluble Cyanide Destruction	99.7	>94.0
Soluble Fluoride Fixation	96.3	94.3
Semi-Volatile Destruction	>88.6	>93.4

[1] Total of 14 semi-volatile compounds listed in Table III.
[2] Corrected for fraction of SPL in kiln feed.

In general, the thermal treatment process, as described above, has been shown to have the versatility and flexibility to detoxify SPL originating from a wide range of technologies, cell capacities and cathode designs. The toxicity of the treated SPL, or kiln discharge, has been greatly reduced. Cyanides are destroyed by oxidation, soluble fluoride salts are converted to relatively insoluble calcium fluoride or fluoride-bearing minerals, and semi-volatile organics are removed by combustion and/or volatilization. The KD was also demonstrated to be non-toxic regarding leachable heavy metals and reactivity (Table IV).

Air Emissions

When treating SPL, the emission of fluorides is always a concern. Air sampling was performed on the exhaust gases from the ESPs and the emission of fluorides was found to be extremely low. Processing temperatures are low enough in the kiln to prevent high generation rates of gaseous fluoride compounds such as HF. Cyanide emissions were also low, as expected.

Gaseous Fluoride Emissions = 0.0019 lb/ton SPL
Gaseous Cyanide Emissions = 0.00078 lb/ton SPL

The emission of particulates is dependent upon the efficiency of the dust removal equipment. Dry ESPs and/or other pollution control equipment will be used to meet air emission standards.

Combustion of SPL

Many of the prior processes developed for the treatment of SPL involve the combustion of the carbonaceous fraction. For this process, the combustion of SPL is not desired. When the temperature within the kiln becomes hot enough to burn the carbon (as noted by large yellow flames emanating from the bed of solids), there is a tendency for the material to agglomerate and form fusion rings on the kiln refractory. For this reason, very little of the carbon is burned within the kiln. Carbon analyses on one occasion have shown the feed blend entering the kiln to be 15.23 ± 1.90 wt.% carbon and the kiln discharge to be 14.54 ± 1.50 wt.% carbon.

Future Schedule

After extensive testing and analyses, Reynolds submitted a petition to the EPA in January 1990 for an upfront or conditional exclusion of the kiln discharge generated by the thermal treatment process from the lists of hazardous wastes. After evaluating the petition, the EPA has proposed that the exclusion be granted as published in the *Federal Register*, Vol. 56, No. 136, July 18, 1991, p. 32993. The EPA concluded that the kiln discharge is non-hazardous with respect to the original listing criteria (cyanide) and, furthermore, was non-hazardous with respect to other factors or criteria that might cause a waste to be hazardous.

An upfront or conditional exclusion is an exclusion for a waste not yet generated provided that the waste meets certain criteria. Based upon EPA's evaluation, the delisting criteria given in Table VI are proposed for the kiln discharge.

The EPA has proposed to exclude up to 300,000 yd^3 per year of kiln discharge which is sufficient capacity to treat all of the presently generated SPL in the United States. Furthermore, the EPA has concluded that the treatment process has the potential to effectively treat SPL from other aluminum producers. However, each new source of SPL must undergo verification testing to ensure that the process can effectively treat that particular SPL.

At the time this paper was written, the proposed exclusion was under review and Reynolds had undertaken detailed engineering studies to construct a RCRA facility to treat approximately 120,000 tons of SPL per year which would generate approximately 300,000 yd^3 of kiln discharge per year.

Table VI. Delisting Levels Proposed by EPA For the Kiln Discharge From the Thermal Treatment Process

NOTE: All concentrations must be measured in the waste leachate from the Toxicity Characteristic Leaching Procedure (TCLP) as outlined in 40 CFK 261.24.

Constituent	TCLP Limit, ppm
Arsenic	0.60
Selenium	0.60
Silver	0.60
Barium	12.0
Antimony	0.12
Cadmium	0.06
Lead	0.18
Chromium	1.2
Nickel	1.2
Mercury	0.024
Beryllium	0.012
Fluoride	48.0
Cyanide	2.4
Acenapthene	24
Benz(a)anthracene	$1.2\text{x}10^{-4}$
Benzo(b)fluoranthene	$2.4\text{x}10^{-4}$
Benzo(a)pyrene	$2.4\text{x}10^{-3}$
Chrysene	$2.4\text{x}10^{-3}$
Fluoranthene	12
Indeno(1,2,3-cd)pyrene	$2.4\text{x}10^{-3}$
Pyrene	12

Conclusions

A process for detoxifying SPL by thermal treatment in a rotary kiln has been developed and operated on a large scale. The cyanides are destroyed by oxidation and the majority of soluble fluoride salts are converted to stable, insoluble CaF_2 by reaction with limestone. An additive is blended with the kiln feed to prevent the agglomeration of the SPL at elevated temperatures. Over 300,000 tons of SPL has been treated successfully using this process.

The EPA has proposed that Reynolds' petition be granted to exclude or delist the treated kiln discharge from the list of hazardous wastes conditional upon the discharge meeting certain criteria. The proposed exclusion would allow for up to 300,000 yd^3 per year of kiln discharge to be delisted, and would allow for the treatment of SPL generated from various sources contingent upon each source passing initial verification testing.