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Conversion of byproduct carbon obtained from spent pot liner treatment plant of aluminum industries to blast furnace tap hole mass[18]

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Abstract: *The paper describes a method for converting carbon powder obtained as byproduct while decontaminating spent pot liner by acid treatment route, into blast furnace tap hole mass. Producing an useful industrial product from waste helps in paying back the cost incurred during decontamination process of spent pot liner and thus improves the overall economics of the process.*
Keywords*: Waste utilization, recovered carbon utilization, blast furnace tap hole mass, spent pot liner.*

I. Introduction

Blast furnace tap hole mass is a prepared muddy material used to close the tap hole of iron making blast furnace. At iron melting temperature the material carbonizes and becomes hard in order to hold the metallostatic pressure inside blast furnace hearth. Since iron gets oxidized at high temperature this tap hole compound is prepared predominantly from carbonaceous material. Further these carbonaceous materials used needs to be semicrystalline in nature in order to withstand high temperature of the furnace. With rising cost of such carbonaceous material used in tap hole compound, it will be advantageous if a source of cheap carbon material matching the properties of carbon material already in use in the tap hole recipe , could be found in order to bring down cost of production of commercial taphole recipe. The aim of this research was to find such a carbonaceous material from an industrial waste which is difficult to dispose because of its toxic contaminants. Such a material chosen for this work is called SPENT POT LINER of aluminum smelter plant.

At present majority of the aluminum smelter plants round the world use Hall-Heraoult's electrolysis process for extracting aluminum metal from molten cryolite. The electrolysis cell used for this purpose constitute large carbon blocks as cathode laid at the bottom and side wall of the cell. These carbon electrodes are known as pot liners and basically made of anthracite, graphite and binder/electrode pitch. Various manufactures uses 20-30% [1] graphite in their recipe in order to meet electrical properties needed for the pot liner. While graphite is a superior electrical conductor than anthracite (which has similar structure to graphite), 100% graphite is never used in the manufacture of pot liners as it is soft and can not withstand turbulent molten cryolite contained in the cell. Anthracite on the other hand provides required mechanical property to the finished pot liner. The prefabricated pot liner produces carbon matrix with short range order. Thus prepared pot liners ultimately contain both crystalline (graphite) and amorphous carbon.

During service molten cryolite slowly gets reduced and the sodium fluoride crystal deposits within the fine crevices of pot liner creating defect spots . As time passes, these crystals grow and exert pressure within these crevices resulting in the propagation of crack. As a consequence, with time the pot liner looses its electrical property and ultimately being discarded. These rejected waste pot liners are called "**spent pot liners"** (in short **SPL**). Spent pot liners are not only contaminated by fluoride but also by other toxic elements such as cyanides (formed at high temperature reaction with atmospheric nitrogen), alkalis and aluminum. Table-1 below shows typical range of the contaminants in such discarded pot liners along with concentration of these toxic elements in SPL carbon powder after decontamination with oxidizing acids.

In practice suitability of a specific component in a commercial recipe is tested by evaluating some gross property of the modified recipe against the production recipe of the compound. For example, in development of foundry chemicals (like mould coating, tundish cover , hot tops etc) which basically a combination of various components in a formulation , various substitutes are being tried with above procedure of gross evaluation of certain properties of the compound in order to determine its suitability. Similarly in present case of developing suitable substitute of carbonaceous material in commercial tap hole compound recipe, following properties are important in order to determine its suitability.

Apparent porosity. This property determines the ease with which gas generated in the tap hole compound during carbonization can escape easily without breaking or decreasing strength of the carbonized tap hole mass. This value is generally maintained in the range 25-35%.

a) Bulk density. This is maintained in the range 1.3-1.6 gm/cc in all commercial recipe in order to match with standard pushing length required by the equipment to fill the tap hole.

b) Permanent Linear Shrinkage. This value is restricted within the narrow range of 0-2.5% in order to guarantee adhesion of the tap hole compound to brick lining and also not to crumple during carbonization.
c) Cold crushing strength. This value is maintained over a broad range of 40-160 kg/cm^2 in order to allow the carbonized tap hole compound withstand metallostatic pressure in the furnace while it is soft enough to be drilled out after the campaign is over by standard equipments.

Table- 1: Typical contaminants in SPL and their concentration after chemical treatment with oxidizing acids.

Contaminants in untreated SPL	*Contaminants in treated SPL*
Fluoride - 6-9%	Fluoride 140-170 ppm
Aluminum - 1-2%	Aluminum 10-15 ppm
Cyanide - 0.2-0.4%	Cyanide 0.1 to 0.2 ppm
Alkali - 7-9%	Alkali 0.5-0.7%

Because of the presence of these toxic elements in large quantities, disposal of spent pot liners in open field poses great environmental risk. Moreover, generation of these spent pot liners by aluminum smelter plants on regular basis being very high (NALCO, Angul itself produces 450 tones spent pot liners per month on the averages) safe disposal of such huge quantity of toxic waste material have been a long standing problem with all aluminum smelters round the world. Efforts have been made to decontaminant these SPL by hydrothermal treatment with partial success as only 45% of the contaminants gets washed out by this process. Concentrated alkalis while leaches away most of the contaminants, extent of removal of the contaminants is very low and can not be translated into actual plant practices. Accordingly majority of smelters at present adopts a policy to crush these spent pot liners to fine powder and burn them in a PF-burner. While this process destroys contaminants in the SPL , it emits pollutant gases such as fluorides and not acceptable by present plant practices. As mentioned earlier, preparation of pot liners comprises use of special carbons and recovery of these valuable carbons in terms of its real commercial value outweighs many times than realizing its calorific value alone. Spent pot liner on the other hand can be decontaminated by treatment with various strong oxidizing acids [2-7]. IMMT, Bhubaneswar, India scaled up such a wet process which extracts all the contaminants in SPL in liquid phase and simultaneously recovers its carbon value as a byproduct. Accordingly the process while decontaminates SPL, generates byproduct carbon powder which can be used to make a number of important industrial carbon products [8-18]. Attempts have also been made to utilize the spent pot liner in producing cement from spent pot liner [19]. In such case the spent pot liner is used as a fuel supplement as well as mineralizing agent in cement kiln. In present experiments the SPL derived carbon powder was used to prepare blast furnace tap hole mass an important industrial product which consumes large volume of semicrystalline carbon. Another reason to find possible use of SPL carbon powder in above product was relative cost of the carbon powder obtained as byproduct from SPL treatment plant. Till now no such attempts have been taken to utilize SPL derived carbon powder as full or partial replacement of carbon in blast furnace tap hole recipe. The properties which are essential in developing a blast furnace tap hole compound are:
a) Flow smoothly when pushed by the clay gun to plug the tap hole.
b) cure within the tap hole during the plug to tap time but without shrinkage to ensure a tight seal
c) be drilled in an acceptable time
d) allow a stable controlled melt stream tap without spray
e) withstand erosion by iron and slag
f) form a stable substrate for next plug
g) Provide a stable and controlled tap hole length. Modern blast furnace work with a tap hole length of 2-3.5 meters.
h) Should be sufficiently porous after curing in order to allow resultant gases to escape easily.

Accordingly commercial tap hole mass is produced from a mixture of refractory materials including carbon powder bonded by tar or synthetic organic binder Carbon powder used in the production of blast furnace tap hole compounds by various commercial manufacturers generally ranges from 10-35%. In order to be able to withstand high temperature of the blast furnace as well as to be oxidation resistant, semicrystalline carbon and sometime carbides are used for this purpose. Compositions of some tap hole compounds made by various commercial manufactures are show in table-2 below.

Table-2: Composition of some commercial tap hole clays

Name of the company	Approximate composition of blast furnace tap hole mass
Saint-Gobain Ceramic: UK	Silicon carbide + carbon = 40 % Silica + Crude Silicon = 15 % Alumina (Bauxite) = 29 % Binder = 16 %
Nippon Crucubles:	Refractory aggregates = 60-85% Graphite + Silicon Carbide = 5- 30 gm Clay = 5-15 gm Binder = 15-25 gm Organic fiber = 0.01-0.75 gm
Riverside refractories (plant of CHZONOW)	Silica = 65 % (Grain size = 0-3 mm) Density = 2.2 gm/cc Total carbon = 20 % Alumina = 10 % Loss of ignition = 10-20 %
Cherepovetsk plant (Russia)(Vanchikov, 1065)	Clay = 16.7 % Ground coke = 50 % Coal tar pitch = 16.7 % Grog powder = 16.6 %
ACC Refractories (Mumbai), India	Alumina = 7.5 % Silica = 90% Iron oxide = 0.8 % Titanium oxide = 0.5 % Graphite powder = 2%

Attempts were made in present experiments to replace the conventional carbon content in tap hole mass recipe with the byproduct carbon powder obtained from SPL treatment plant as mentioned above. The incentive for such replacement comes from the relatively low cost and abundant supply of carbon powder from SPL treatment plant. The other advantage is that sell of these byproduct carbon to other industries will pay back fully or partially the cost incurred in decontaminating SPL in the above treatment plant.

II. Experimental

The spent pot liner derived carbon powder was first characterized through studies involving scanning electron microscopy, differential thermal analysis, x-ray diffraction and ash determination. While ash was found to vary between 5-10% (for handpicked first cut SPL), alumina in ash found to vary 20-52% and silica 42-72%, while loss on ignition (LOI) was 1-2%.

Experiments were designed to study possible application of SPL derived carbon powder in making blast furnace tap hole mass using two separate recipes containing 23% and 26% of SPL derived carbon powder. Suitability of a particular blast furnace tap hole recipe is evaluated by certain standard tests both at room temperature and after curing the compound at high temperature. These properties include apparent porosity, bulk density, permanent linear shrinkage, and cold crushing strength.

Liquid resin binders such as Resol and Novolac are used for preparing the blast furnace tap hole compounds. In this case they were prepared as follows:

Resol : 50 gm phenol is added to 60 ml formalin and 1.06 gm NaOH. The mixture was stirred for about 15 minutes to make it homogeneous and then heated at constant temperature ($80\text{-}90^0$ C) till the gas bubbles comes out the heating mixture. The mixture was cooled for 5-10 minutes at room temperature and then stored in an air tight bottle in a freezer.

Novolac : This resin was prepared by adding 50 gm phenol to 32 ml formalin and 5 ml hydrochloric acid (commercial grade). The mixture was stirred for about 15 minutes to make it homogeneous and then

heated to constant temperature of 80 -90^0 C and hold at this temperature until bubbles starts coming out. It was then cooled for 5-10 minutes at room temperature and then kept in refrigerators until use.
Commercial binders thus prepared do not contain stabilizer and added to the tap hole clay as soon as it is prepared.

Other solids components such as refractories, used in the recipe were prepared as follows. Refractory raw materials such as alumina, silica, silicon carbide, titania, ferric oxide etc were first dried at 120^0 C for 2 hour in an oven and sieved through -100 BS mesh. The dried and sieve mixture was then put into a Muller mixture into which liquid ingredient (like binder) were added with constant stirring. This process continued for about 20 minutes to make a homogeneous clay. Viscosity of the resultant clay was simultaneously fixed by the ratio of liquid to solid mixture in the Muller mixture.

Property of the tap hole mass after high temperature curing was measured first by compacting 100 gm of above clay in an Universal Tensile Machine using steel die and applying a force of 200 kg/cm^2. The compact thus prepared was put into a steel cylinder and packed with coke and then fired at about 1000^0 C for 2 hours in ambient (atmospheric) pressure of the furnace. The drillabilty, apparent porosity, bulk density, permanent linear shrinkage, and cold crushing strength were determined in order to adjudge its suitability for application as blast furnace tap hole compound

III. Result and discussion:

Properties of the SPL derived carbon powder as measured in our laboratory, is shown in Table 3 below. X-ray diffraction analysis of the SPL derived carbon powder is shown in Figure-1 while results of Scanning Electron Micrograph is shown in Figure-2 below. Results of differential thermal analysis with above carbon powder is shown in Figure-3. Figure-1 clearly shows that the carbon powder derived from SPL is crystalline in nature because of its clear cut peaks but not as sharp as natural flaky graphite. Thus the carbon powder obtained from SPL treatment is semicrystalline in nature. Crystallinity of the SPL derived carbon powder is further confirmed from Figure-2 which shows clearly disposition of geometrically shaped crystals under scanning electron micrography. Thermal behavior of such powder is exemplified in Figure-3 which compares its rapid oxidation temperature around 600 ^{o}C when compared to natural graphite. This high temperature sustainability towards oxidation makes it's a suitable candidate for application in the tap hole compound recipe.

Table – 4 shows the values obtained for above mentioned properties of blast furnace tap hole compositions containing 24% SPL derived carbon powder (composition 1) , while Table-5 shows the same results obtained with composition-2 containing 32% SPL carbon powder.

X-ray diffraction and Scanning Electron Micrography results as mentioned above for SPL derived carbon powder, indicates that these carbon powders are semicrystalline in nature and could be a possible good candidate for use in blast furnace tap hole mass recipe. Semicrystalline nature of carbon powder imparts thermal stability to the carbon powder. Differential thermal analysis when compared with graphite powder indicates high oxidation resistance of the SPL carbon powder at high temperature. These results thus points to possible use of the carbon powder in blast furnace tap hole recipe.

After preparation of the two recipes (composition -1 and composition -2) and curing them at high temperature, properties which are necessary for blast furnace tap hole compound, as mentioned above, were evaluated . Table 4 and 5 shows these results and Table-6 shows the same properties generally found with some commercial tap hole compounds. Comparison of these two tables indicates that SPL derived carbon powder can be used successfully in producing blast furnace tap hole compounds upto at least 30 % replacement level. Increasing SPL carbon content further decreases apparent porosity and increases permanent linear shrinkage beyond acceptable limit. Further increasing SPL carbon content in the recipe calls for increase in resin content to maintain desired cold crushing strength and drillability but at the same time permanent linear shrinkage and apparent porosity goes beyond acceptable limit.

Accordingly it is concluded that carbon powder derived from SPL treatment can be used to replace conventional carbon in commercial blast furnace tap hole mass compositions.

Table 3: Properties of SPL derived carbon powder.

Fixed carbon	80% and above (Protocol: IS 3150)
Ash content	6-10% (Protocol: IS 3150)
Moisture	1.2% average (Protocol: IS 3150)
Bulk density	525.5 gm / lit (Protocol: IS 877/1989)
Iodine number	920 mg/gm (Protocol: ASTM D1510)
Methylene blue	155
Particle size distribution	0-3mm (plant discharge)

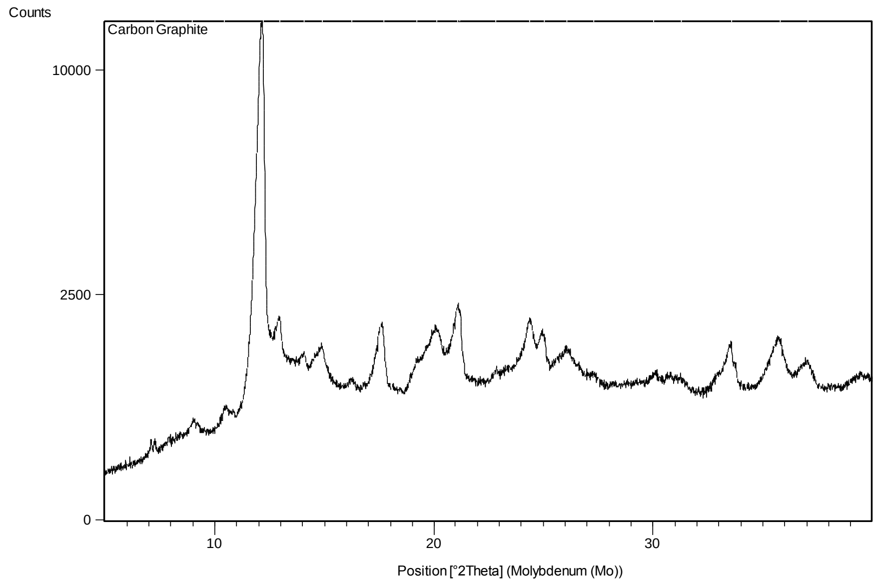

Figure 1: X-ray diffraction of SPL derived carbon powder

Peak list:

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
7.2627	137.20	0.0472	5.61092	1.26
8.9857	258.78	0.3149	4.53663	2.37
10.4520	368.48	0.1574	3.90160	3.38
12.1995	10898.34	0.0630	3.34440	100.00
12.9837	1637.99	0.0630	3.14319	15.03
14.0871	1020.70	0.0945	2.89808	9.37
14.8936	1135.16	0.1889	2.74197	10.42
16.2422	592.95	0.1889	2.51565	5.44
17.6866	1273.04	0.1260	2.31164	11.68
19.1980	806.22	0.1889	2.13117	7.40
20.1282	1320.46	0.3149	2.03362	12.12
21.1090	1836.65	0.1344	1.93622	16.85
21.2307	1597.75	0.0768	1.93689	14.66
22.8250	569.59	0.2304	1.79238	5.23
24.3763	1396.86	0.3456	1.67988	12.82
25.0592	1063.39	0.3072	1.63480	9.76
26.0774	827.39	0.3840	1.57201	7.59
27.3126	411.05	0.4608	1.50217	3.77
30.0432	357.54	0.3840	1.36837	3.28
31.2868	259.93	0.9216	1.31526	2.39
33.5645	780.09	0.0768	1.22832	7.16
35.7889	759.42	0.3072	1.15425	6.97
37.0546	369.46	0.4608	1.11614	3.39

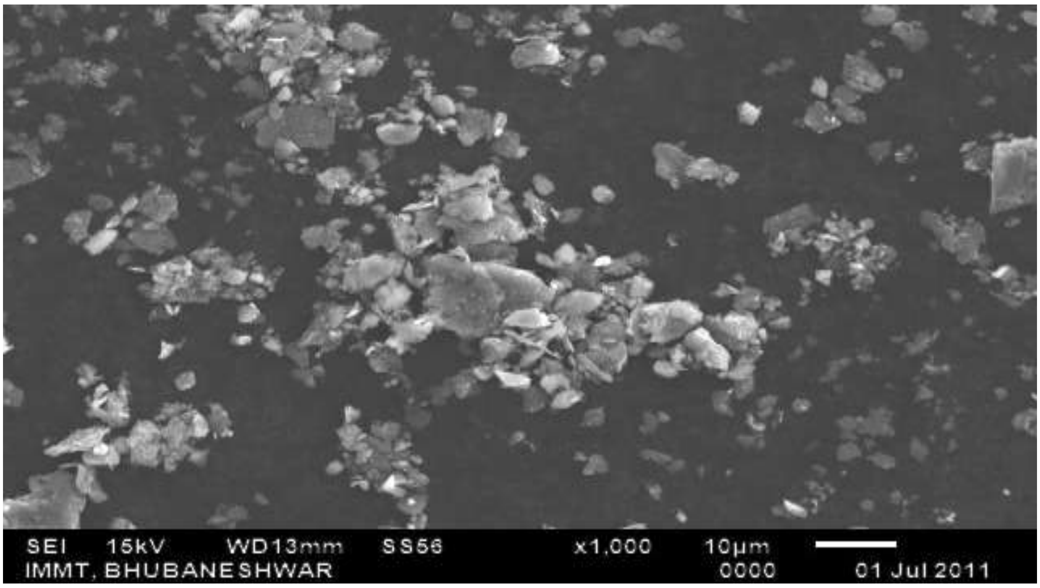

Figure 2: Scanning electron micrograph of SPL carbon powder.

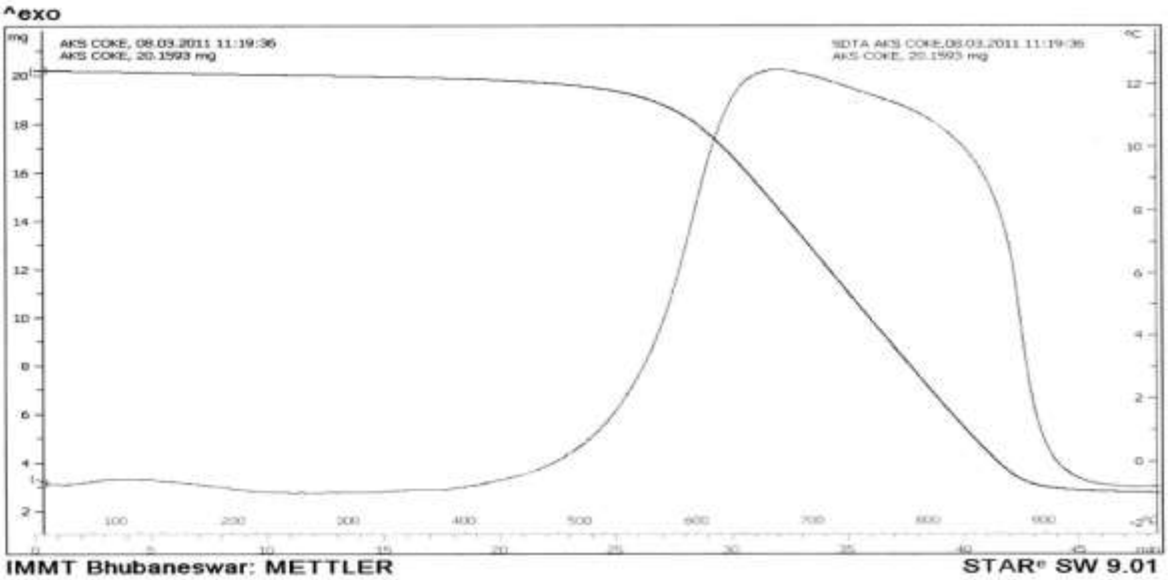

Figure 3: Differential thermal analysis of SPL carbon powder (Reference: graphite)

Table 4 : Properties of cured tap hole clay (Composition -1)

Ingredients	%	Apparent porosity	Bulk density	Permanent linear shrinkage	Cold crushing strength
Alumina	28.35				
Silica	4.51				
Silicon carbide	13.5				
Titania	1.38				
Fe_2O_3	1.42				
Carbon from SPL	23.86	27.65%	1.38gm/cc	2.39%	161kg/cm^2
Liquid resin	16				
LOI (Solids)	1.24				
Moisture	0.52				
Solid resin	Nil				

Table 5: Properties of cured tap hole clay (Composition -2)

Ingredients	%	Apparent porosity	Bulk density	Permanent linear shrinkage	Cold crushing strength
Alumina	28.35				
Silica	4.51				
Silicon carbide	Nil				
Titania	1.38				
Fe_2O_3	1.42				
Carbon from SPL	31.61	26.15%	1.61gm/cc	2.41%	153kg/cm^2
Liquid resin	20				
LOI (Solids)	1.24				
Moisture	0.76				
Solid resin	Nil				

Table-6: properties of some commercial tap hole compounds.

Company Name	Apparent porosity %	Bulk density	Permanent Linear Shrinkage (%)	Cold crushing strength
Sino-global sourcing & supply Ltd.	25-35	2.30 g/cc	1.0	61.5 kg/cm^2
Satguru Refractories India	25-35	2.8 g/cc	-0.8 at 900 ^{0}C -0.1 at 1400^{0}C	75 kg/cm^2
ACC Refractories India.	25-35	1.54 g/cc	+2.00	35 kg/cm^2

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