GREEN, SAFE AND CLEAN CARBON PRODUCTS FOR THE ALUMINIUM ELECTROLYSIS POTS

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Abstract

Carbon products used in aluminium electrolysis pots are generally based on coal-tar pitch or resin binders. Coal tar pitch is considered by the new European chemicals legislation REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) as very high concern product, and it is carcinogenic classified. Phenol, a typical component of resin binders used in carbon products, is also carcinogenic classified. In face of these hazards, solutions that guarantee a clean and safe environment for the workers have to be found. Last year a 100% clean ramming paste NeO[2] has been introduced, based on a new binder type containing no CMR product (CMR: carcinogenic, mutagenic or toxic for reproduction) and no hazardous substance. This paste was fully anthracitic. Since then, Carbone Savoie made developments to complete its Green range with a 100% clean semi-graphitic grade of ramming paste, using the same type of binder and with a 100 % clean glue, which could be used at different locations in the pot. Characteristics of these new products will be presented.

Introduction

Finding ways to substitute carcinogenic products becomes an Environmental Hygiene and Safety project for most of the industries, especially to protect the health of the workers, wherever they stand, at the production sites, but also at the end-users sites.

Situation of today

Carbon products used in the aluminium electrolysis pots include anode and cathode blocks, but also sidewall blocks, ramming pastes, and glues. Those materials are generally based on particles linked with a binder. The binder originates from the coal tar pitch family for most of the cases. Coal tar pitch is carcinogenic classified, under the category 1 by the International Agency for Research on Cancer, which means it is considered as carcinogenic for humans. It is now on the list established by REACH of products with very high concern. It contains many Polycyclic Aromatic Hydrocarbons components, the most hazardous of them being the heaviest, emitted as particulates. Benzo[a]pyrene, which is the main traceur for the Polycyclic Aromatic Hydrocarbons, is also classified carcinogenic.

Many studies have been done to substitute pitch-based binders, especially in ramming pastes, as people are exposed to hazardous emissions during the ramming operation. Last year a new anthracitic paste, based on a non-hazardous natural binder, has been presented [1]. The use of such binder in a semi-graphitic paste allows combining the specific properties of semi-graphitic paste with the advantage of removing carcinogenic and even hazardous substances.

Another type of binder which is used in the carbon products, mainly glues, is phenolic resin. Compared to pitch-based binders, phenolic resins present a lower carbon yield, but which is among the highest in the resin family, and depending upon the phenol / formalin ratio, they can either cure at temperature with a catalyst, or cure at room temperature with a hardener. Since 2009, phenol, a component of the phenolic resins, is also classified carcinogenic, and there is also a need to find a substitute for such binder. Moreover such system usually needs formaldehyde-based components, and formaldehyde is also hazardous, classified as harmful. A new glue has been developed, which is not classified hazardous by the European Union.

Characteristics of the semi-graphitic paste developed

Presentation of the products:
The main objective of semi-graphitic paste, compared to fully anthracitic ones, is the increase of the thermal conductivity of the material. It could be an improvement in some designs to help increasing the heat flux across the sides, and thus cooling the inside of the pot, to get a better frozen bath ledge.

As for cathode blocks, a way to increase the thermal conductivity of the carbon product (or to decrease the electrical resistivity) is to add graphite in the formulation.

Different types of ramming pastes have been studied, some are industrial ones, and the others have been prepared in laboratory, with a small mixer. The description of the range studied is given in Table I.

Table I: Presentation of the pastes studied. AN: anthracitic, SG: semi-graphitic, CTP: coal tar pitch based, N: natural binder. Production: "ind" for industrial and "lab" for laboratory.

Reference	A	B	C	D	E
Filler	AN	AN	SG	SG	SG
Binder	CTP	N	CTP	CTP	N
Production	ind	ind	ind	lab	lab

Characteristics of the paste:
Several types of measurements are performed on ramming pastes, either to determine their rammability, or to get their physical characteristics at room temperature, or to determine the evolution of some of their properties versus temperature, up to 1000°C, which will be their final temperature in pots.

The densification curve of the paste is obtained with a Fischer Sand Rammer equipment (see picture 1), which automatically performs 250 strokes to densify the paste. The follow-up of the height of paste densified in a mould of 50 mm diameter allows

calculating the geometrical green density of the paste versus the stroke number.

Figure 1: Fischer Sand Rammer equipment

The semi-graphitic paste E that has been developed presents a target ramming temperature of 20°C. The curves below on Figure 2 allow comparing this new paste, with another paste D based on the same particle formulation but with a standard type of binder, originated from coal-tar pitch family. Both pastes have been prepared in laboratory and are compared to the industrial fully anthracitic pastes A and B, and to the semi-graphic one C.
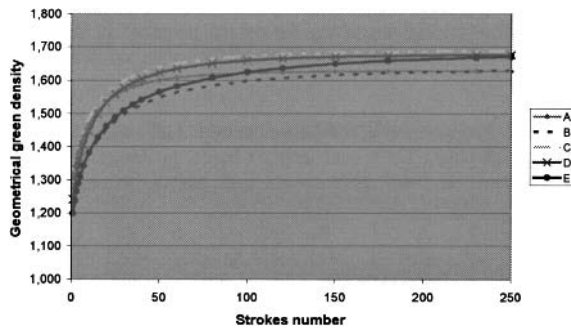

Figure 2: Densification curves given by the Fischer Sand Rammer on pastes A, B, D and E.

The maximal green density is given by the plateau value of the curve. It can be seen on Figure 2, that both semi-graphitic pastes C, D and E present a higher maximal green density than the anthracitic pastes A and B. It is in line with the known effect of graphite. The maximal density reached for pastes C, D and E is similar, and the same observation could be done on pastes A and B, meaning that the binder nature does not affect the level of density. But the binder nature which is the same in pastes B and E, has an effect on the slope of the curves, which is similar for both pastes and less steep than the slopes of pastes A, C and D which contain a coal-tar pitch based binder. It means that pastes B and E require more energy than pastes A, C and D to obtain the maximal density. The rammability index N2 is calculated by assuming a Weibull distribution, according to the ISO standard 17544:2004. The higher N2 is, the dryer paste is, and requires more energy to be densified. Table II presents the rammability index N2 obtained for the different pastes, and the maximum density given by the Fischer Sand Rammer. The two pastes B and E with a natural binder have a higher rammability index than pastes A and D, which differ in the binder nature only, but they also present a higher maximum density.

Table II: Typical rammability index N2 and maximum green density D max, for the different ramming pastes

	A	B	C	D	E
N2 (strokes)	51	72	58	54	115
D max	1.622	1.641	1.690	1.680	1.692

Larger samples 90 mm in diameter, 150 mm height, have been densified in a mould with a hand rammer, and baked at 1000°C to obtain the physico-chemical characteristics at the green stage and after baking. Table III summarizes the main properties.

Table III: standard characteristics for the different ramming pastes

	A	B	C	D	E
Green density	1.60	1.62	1.68	1.67	1.66
Baked density	1.44	1.39	1.48	1.43	1.33
Volumic expansion (%)	1.5	2.6	1.4	3.2	6.8
Crushing strength (MPa)	17	19	16.8	15.9	12.2

Laboratory samples D and E have been prepared with the same binder level, higher than the one of the industrial paste C. That could explain that the densities are lower, and the volumic expansions much higher. But all the semi-graphitic pastes are higher in density than the anthracitic ones, due to the graphite content. The level of the other properties does not vary significantly with the graphite content.

The effect of the binder nature could be seen for respectively the anthracitic pastes and the semi-graphitic ones. The new clean binder tends to give a higher volumic expansion and a lower density after baking, probably linked with a different departure of volatile matters.

The linear expansion during baking curve has been determined on the different samples densified in the Fischer Sand Rammer equipment. This curve is determined during the baking of a paste at a temperature increase rate of 180°C/mn as fixed in the ISO 14428 standard. Figure 3 allows comparing the different grades of paste, each curve being the average of two individual curves.
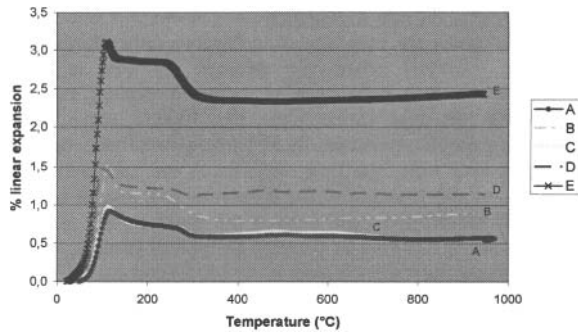
Figure 3: Linear expansion during baking curve of the different pastes.

All pastes present a positive linear expansion up to 950°C. The peak value at around 3% for the E paste related to the high volumic expansion measured between the green stage and after baking at 1000°C. By optimizing further the binder level, the curve could be easily translated to lower levels, close to those of the other pastes. B and E pastes, based on the new clean binder, exhibit a very interesting shape of curve, which slightly expands after 500°C, instead of shrinking.

Both this pattern of expansion between 500 and 950°C, and the corresponding rather high volumic expansion value, are in the good direction to decrease the risk of infiltration in pots.

Impact of the thermal conductivity level:

The thermal conductivity of each paste has been measured with the Kohlrausch method at a fixed temperature of 30°C. The evolution of thermal conductivity with temperature has been determined according to the same method [2, 3], inside a special furnace working under vacuum to get only axial conduction and avoid radial conduction or convection phenomena (see Figure 4). The sample is 20 mm in diameter and 100 mm in length. A shield is put around the sample to make the radiation component negligible.
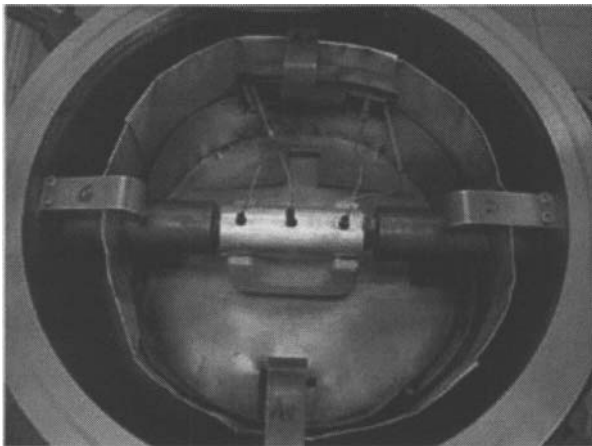

Figure 4: Vacuum chamber of the equipment to measure the thermal conductivity in temperature, with the sample located in the middle.

The values of the thermal conductivity at 30°C and 1000°C for the different pastes are given in Table IV. The range is the same for the semi-graphitic pastes, between 9 and 12 W/mK, higher than those of the anthracitic pastes which are 5-6 W/m.K. The binder nature does not significantly affect the results.

Table IV: Thermal conductivity (W/m.K) at 30°C and 1000°C for the different ramming pastes.

Thermal conductivity (W/m.K)	A	B	C	D	E
30°C	6	5.6	10.3	9,7	9.1
1000°C	10.8	11.3	15.5	13.9	15.7

The evolution of thermal conductivity versus temperature is represented in Figure 5. Generally the points fit with a quadratic relation versus temperature, in some cases it is close to a linear relation. The general trend for all the pastes is an increase of the thermal conductivity with temperature. The difference observed at 30°C between anthracitic and semi-graphitic pastes is kept at 1000°C.
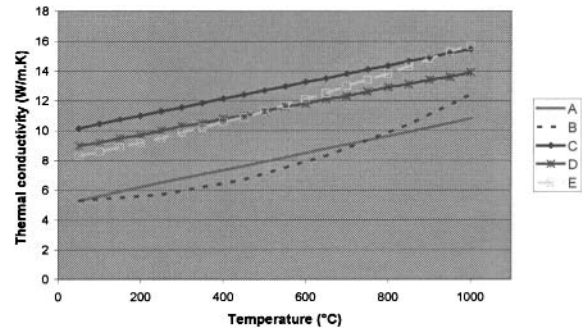

Figure 5: Thermal conductivity versus temperature.

The impact of moving to semi-graphitic pastes on the thermal balance of the pot could be illustrated by thermal modelling. Figure 6 below shows a reference case a) in a high-amperage pot with a 20°C anthracitic paste similar to A. Case b) corresponds to the use of a semi-graphitic paste. The location of the frozen bath ledge is indicated by the thick black line. With semi-graphitic paste, the frozen bath ledge covers more of the ends of the cathode blocks, and thus decreases the risk of infiltration at the paste-block interface. The temperatures on the shell at the levels of the sidewalls and cathode blocks are higher, illustrating the better heat flow. But the temperature profile at the bottom of the cathode or at the collector bar level is maintained. The use of semi-graphitic paste is thus a good alternative to increase the frozen bath ledge thickness, and especially to have this ledge covering the big joint and the end of the cathode. It could help increasing the amperage without increasing the risk of infiltration.

In conclusion, the use of semi-graphitic paste could help achieving a good thermal balance in the pot. There is a need to substitute hazardous products by non-hazardous ones for health reasons. By replacing coal-tar pitch based binder by a natural binder, the properties of the pastes are maintained, and even improved regarding the behaviour of expansion during baking. Such clean pastes may require more energy during ramming, according to the rammability index, but so far the experience on

the anthracitic clean paste does not show a difference in total ramming duration compared to standard pastes.
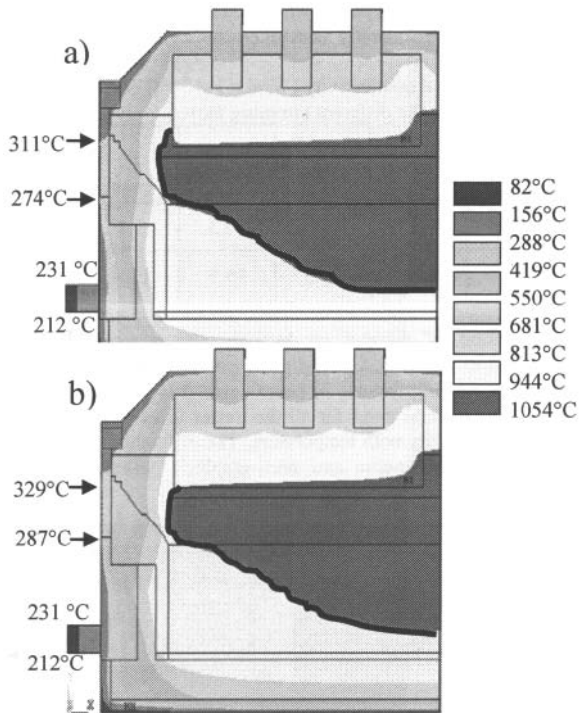

Figure 6: Thermal modelling of a high amperage pot with a) the reference case with a 20°C anthracitic paste, and b) a 20°C semi-graphitic paste.

Characteristics of the new glue developed

The glue which is studied is used to join either cathode blocks, or carbon preformed blocks with silicon carbide slabs.

Functions of the glue
The main functions required by such glue are:
- easiness of preparation
- easiness of spreading on carbon, graphite or silicon carbide surfaces
- the duration for which the glue could be used. It should be at least one hour at ambient temperature
- the hardening or curing time of the glue should be short enough to allow the handling of the assemblies. Generally a curing time of twenty four hours is considered as a maximum whatever the ambient temperature is.
- after curing, the mechanical strength of the assembly should be high enough to allow the handling and transportation of the assemblies, without any failure.
- in the pot the glue will be baked at a high temperature, 1000 °C maximum, and should keep some mechanical properties after baking, in order that the integrity of the assembly is kept.
- the storage time of the glue before use should be long enough, at least several months and possibly up to one year, at various ambient temperatures.

Advantages of the new formulation
Generally glues are based on resin binders, either furfurylic or phenolic. Phenolic resins are amongst the best to find a thermosetting resin fully cured at room temperature that could also stand very high temperatures, like 1000°C, while keeping good mechanical properties. Such binders could also be stored during a long time, one year, sometimes one year and a half, without any deterioration of the properties. But phenol has been classified carcinogenic and even if the trend on the market of phenolic resins has been to decrease the phenol content, it is still present in the formulae. Moreover to get a good curing at room temperature, formaldehyde polymers are classically used, and formaldehyde is classified as harmful.

The new formulation which has been developed is not based on a resin binder, but on a hydraulic binder. It comes from the mortar family, requiring just water, but with adjustments in order to fulfil the requirements listed in the previous paragraph.

As such, the formulation developed is not classified as hazardous according to the European regulations.

Instead of having two components to mix, with one based on phenolic resin, which is hazardous for the user but also a hazardous component to transport, people will receive a dry mix only, which will be poured into water.

Characteristics of the new glue
Several formulations have been tested, based on different dry mixes, with various levels of water content, and at various ambient temperatures ranging from 10 to 35°C.

To get quickly a homogeneous mixture, the best is to pour the dry mix into the water, and not the opposite. The dry mix spreads easily in water, whereas the water has difficulty to penetrate into the dry mix. When pouring the dry mix into the water, it gives some dust, but the mixing takes less than one minute. The mixing tool could be the same as for paint (Figure 6), with a variable rotating speed for the engine.
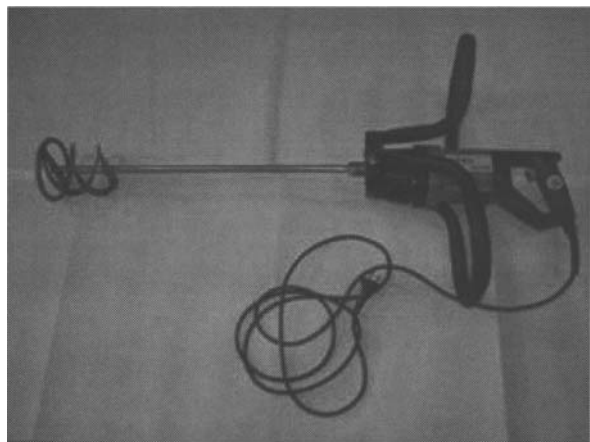

Figure 6: Tool for mixing the glue.

The curing time or the hardening time could be determined at different temperatures with a Trombomat equipment, which gives the evolution of the apparent viscosity of the mixture versus time.

It also gives an indication of the duration during which the glue could be used before getting too viscous to be easily spread.

Compared to the reference formula based on phenolic resin, the new glue presents a very different behaviour: it hardens suddenly, with a very steep slope, whereas the phenolic resin-based glue is slower to cure (cf Figure 7). At 23°C for example, the new glue could be used during approximately 2.5 hours, but after that it will become hard.
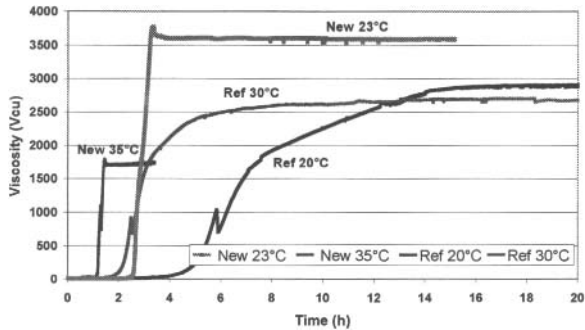

Figure 7: Apparent viscosity of the new glue and the reference glue for different levels of temperature.

To characterize the mechanical strength of the assembly, two carbon slabs are glued, with a pressure applied during 10 min in the centre of the assembly (see Figure 8). Cores are taken in the assembly 24 hours later and broken in a flexural test. The core size is 50 mm in diameter and 130 mm long. A 3-point bending test is performed with the load applied directly on the glue joint. The level of flexural strength indicates the resistance of the joint. The fracture pattern shows if the failure occurs inside the glue (cohesive fracture) or at the interface between glue and carbon (adhesive fracture). The flexural strength is measured with the glue at the green stage, or after treating the cores at 1000°C, so with the glue baked.

Figure 8: Gluing bench with two carbon slabs glued with a joint. Pressure is applied at the centre of the assembly.

The effect of gluing temperature has been checked on different assemblies on the same formulation of the new glue, with a fixed water content. Six cores have been taken in each assembly, with four cores to measure the flexural strength with the glue at the green stage, and two cores to measure the flexural strength with the glue baked at 1000°C. Table V gives the average results and also the standard deviation between the four cores at the green stage.

Table V: Flexural strength of the new glue at the green stage and after baking at 1000°C.

Flexural strength (MPa)	green stage		baked
	average	standard deviation	average
10°C	6,4	0,37	0,3
23°C	6	1,29	0,2
35°C	9,6	1,51	0,4

The results at the green stage are of the same order of magnitude than the typical value of 6.9 MPa of the reference glue based on phenolic resin. After baking the reference glue is generally between 1 and 2 MPa, higher than the new one. But the new glue formulation presents the advantage of increasing in mechanical strength with time. All the values determined 24h or even some days after gluing are underestimated, compared to what can be obtained two months later. Most of the time the assemblies will wait at least one or two months before being baked in the aluminium pot, during the pot preheating. Therefore even values below 0.5 MPa after baking, will be considered acceptable as soon as they are above zero. Some measurements have been made 4 hours after gluing, at a room temperature of 23°C. Even if the glue is hard at that time, it is more brittle and the flexural strength at the green stage is average 2 MPa, and after baking, the results are null. Consequently it is recommended to wait 24 hours after gluing before handling the assemblies. But a study will be done to see if by increasing the temperature of the assembly after gluing, it helps reducing the time during which the assembly should not be moved.
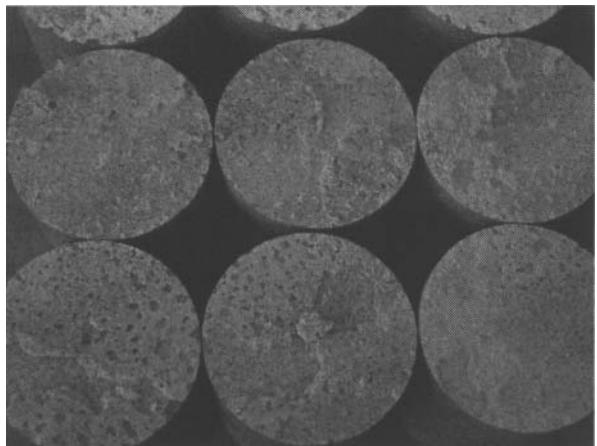

Figure 9: Failure pattern after 3-point bending test. The failure occurred in the glue itself.

After the flexural test, the failure pattern which is observed is cohesive, inside the glue (see Figure 9). Sometimes the cores even break in the carbon, instead of breaking in the joint. The interface between glue and carbon could be considered as resistant.

The new glue developed does not contain any hazardous component. Phenol and formaldehyde components have been totally removed from the formulation. The new glue presents some other advantages as it only requires water in which the dry mix is poured. The mixing is a quite easy operation. The glue hardens quickly and presents good levels of mechanical strength. A way to reduce the waiting time of presently 24 hours, before handling the blocks, will be studied by using the temperature. The storage time of the dry mix has also to be evaluated.

Conclusion

After NeO², a 100% clean fully anthracitic ramming paste, with no hazardous component, a 100% clean semi-graphitic paste is under development in Carbone Savoie, with a higher thermal conductivity which could help modifying and optimizing the thermal balance in the pot. The use of the new binder brings advantages on the expansion during baking behaviour of the paste. A new and 100% clean glue is also presented with no phenol, no formaldehyde and no hazardous component. The levels of the characteristics are promising. Some further studies will be made to determine the storage life of the dry mix and to decrease the waiting time before handling the assemblies.

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