Performances of green and eco-friendly ramming pastes in EGA pots

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Abstract

Consistent and high quality ramming paste products, installed according to optimised procedures, are required for improved operation and longer pot life. However, ramming paste used to be a hazardous product and needed special precautions for handling and application. A 100 % eco-friendly cold ramming paste has been developed by Carbone Savoie and tested at Emirates Global Aluminium (EGA) sites. A test has also been developed by Carbone Savoie to follow-up, identify and quantify emissions during the baking of paste up to 1 000 °C. Physico-chemical characteristics of various pastes are presented, together with their composition in polycyclic aromatic hydrocarbons (PAH) and volatile organic compounds (VOC), determined by an accredited laboratory and the results of emissions during paste baking. The results of pot operation at the EGA sites show no harmful impact on pot preheat, early operation or regular operation performance. Pot performance data are given for comparison. Th new paste offers a green and clean alternative to harsh chemicals typically associated with the industry.

Keywords: Ramming paste; eco-friendly cold ramming paste; PAH; characteristics; pot performances;

1. Introduction

Ramming paste plays an important role in the pot, ensuring pot tightness regarding metal infiltration at the block/paste interface. The installation of ramming paste is a heavy operation that could lead to technical and quality issues, as well as health, safety and environmental issues. In recent years, ramming paste producers have developed eco-friendly (EF) products to reduce PAH content and Carbone Savoie has been the first to introduce a 100 % clean paste, which has been used at EGA sites. A test has also been developed by Carbone Savoie to follow-up, identify and quantify emissions during the baking of paste up to 1 000 °C.

Several pastes used at EGA's sites were fully characterised to obtain their physico-chemical properties, as well as their composition in PAH and VOC, and their emissions during baking. The results of pot operation at the EGA sites are also presented.

2. Ramming pastes presentation

Five types of ramming pastes have been studied, labelled A, B, C, D and E. They are either 100 % anthracitic pastes or semi-graphitic, and are based on various types of binder, which affects the PAH content of the paste and the emissions during baking. The range of working temperature of the pastes is indicated in Table 1, together with their expiry date. Paste B is NeO^2 and paste E is $CleO^2$ of Carbone Savoie.

Table 1. Working temperature range and expiry dates of the five pastes studied.

Sample ID	A	B	C	D	E
T range (°C)	20 to 40	10 to 50	17 to 42	20 to 40	10 to 50
Expiry date	End of Sept'2015	End of July'2015	End of Jan'2016	End of July'2015	End of Mar'2016

2.1. Chemical composition

The five pastes were sent to an accredited external laboratory to evaluate their chemical composition in terms of PAH and VOC. A list of 50 VOCs could be analysed. The PAH extracted were analysed by gas chromatography associated with a mass-spectrometer. Table 2 gives the results for 17 PAH, the most commonly measured; together with BTEX and VOC. For VOC, only the species detected at least in one of the pastes, are listed.

Table 2. PAH, BTEX and VOC composition of the pastes in mg/kg.

Pastes	A	B	C	D	E
Component (mg/kg)					
Fluoranthene	1529	< 10	1817	1255	< 10
Benzo(b,j)fluoranthene	54.1	< 10	37.2	1745	< 10
Benzo(k)fluoranthene	16.7	< 10	11.2	392	< 10
Benzo(a)pyrene	**59.1**	**< 10**	**38.4**	**1373**	**< 10**
Indeno-pyrene	69.2	< 10	53.8	459	< 10
Benzo(g,h,i)perylene	143	< 10	88.5	1294	< 10
Naphtalene	663	< 10	492	14137	< 10
Acenaphtene	13394	< 10	16481	13196	< 10
Fluorene	7798	< 10	12327	2863	< 10
Phenantrene	4683	< 10	5587	882	< 10
Pyrene	808	< 10	1087	1088	< 10
Benzo(a)anthracene	51.6	< 10	59.7	892	< 10
Chrysene	45.7	< 10	54.9	1088	< 10
Acenaphtylene	< 10	< 10	12.9	31.7	< 10
Dibenzo(a,h)anthracene	21.5	< 10	18.3	190	< 10
Anthracene	541	< 10	554	155	< 10
BbNT	< 10	< 10	10.1	122	< 10
PAH total	**29 877**	**-**	**38 730**	**41 163**	**-**
Benzene	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
Toluene	< 0.05	< 0.05	0.23	< 0.05	< 0.05
Ethylbenzene	0.15	< 0.05	0.55	0.21	< 0.05
Xylene	0.19	< 0.10	0.54	0.61	< 0.10
BTEX total	**0.34**	**-**	**0.78**	**0.82**	**-**
dichloromethane	0.38	0.31	0.37	0.4	0.32
trimethyl-1,2,4 benzene	0.07	< 0.05	0.1	0.68	< 0.05
trimethyl-1,3,5 benzene	0.1	< 0.05	0.18	1.1	< 0.05
n-butyl benzene	0.14	< 0.05	0.2	0.26	< 0.05
cumene	< 0.05	< 0.05	0.1	0.08	< 0.05
n-propyl benzene	< 0.05	< 0.05	0.06	< 0.05	< 0.05
styrene	< 0.25	< 0.25	< 0.25	0.28	< 0.25
cymene	< 0.05	< 0.05	< 0.05	0.1	< 0.05

For pastes B and E, neither PAH nor BTEX could be measured. Only dichloromethane could be detected, as in all pastes. Dichloromethane is the usual solvent for chemical analyses and these values could correspond to some pollution in the analytical equipment.

Pastes A and C present a rather similar PAH and BTEX profile, with a high amount of acenaphtene, fluorene and phenantrene (by descending order). Paste D presents the highest level of PAH and BTEX, and also by far the highest level of Benzo(a)pyrene (BaP). The level of BaP shows clearly that

B and E are 100 % clean pastes; A and C are EF ramming pastes; and paste D is a standard ramming paste based on coal tar pitch [1].

An Equivalent Toxicity Factor (ETF) can be calculated based on the knowledge of the health impact of the different PAH molecules [2], by using a Relative Potency Factor (RPF) that gives more weight to the most dangerous molecules. The RPF is given in Table 3, and the results of ETF calculations for pastes A, C and D are given in Table 4, compared to the typical ETF already published for some pastes [1].

Table 3. Relative Potency Factor [2]

	RPF
Naphtalene NA	
Fluorene FL	0.001
Phenantrene PH	0.001
Anthracene ANT	0.01
Fluoranthene FA	0.001
Pyrene PY	0.001
Benzo(a)anthracene BaA	0.1
Chrysene CH	0.01
Benzo(b)fluoranthene BbFA	0.1
Benzo(k)fluoranthene BkFA	0.1
Benzo(a)pyrene BaP	**1**
Benzo(g,h,i)perylene BjhiP	0.01
Dibenzo(a,h)anthracene DiahA	1
Indeno-pyrene IP	0.1

Table 4. Equivalent Toxicity Factor according to [2] for pastes A, C, D.

Type of paste	A	C	D	Tepid	Cold	Tepid EF
ETF (ppm)	121.9	100.7	1943	2500	2300	300

The values of ETF confirm that paste D is close to a standard cold paste based on coal tar pitch binder, whereas pastes A and C are close to EF pastes. The calculation of ETF is thus more discriminating than the simple mathematical sum of PAH species.

2.2. Paste densification

To help in paste comparisons, all pastes were densified at the same temperature of 30 °C, which is intermediate and inside each temperature window (see Table 1). Densification was achieved either with Fischer Sand Rammer (FSR) equipment at 250 strokes, which gives samples of 50 mm diameter and about 50 mm high; or with a hand-rammer, which gives samples of 90 mm diameter and about 150 mm high. With the FSR, the amount of paste involved is 180 g, whereas with the hand-rammer it is 1 500 g for a standard sample and 1 700 g for samples devoted to electrolysis testing.

On the small FSR samples, the green geometrical density and ability of the paste to be densified can be evaluated, together with the N2 index. Some samples were heat-treated at 950 °C to determine the linear expansion curve versus baking temperature. Other samples were used to follow-up the emissions of paste during baking up to 1 000 °C.

The large samples densified with a hand-rammer were all baked at 1 000 °C to determine physic-chemical properties after baking, some of them being measured at 1 000 °C and possibly under electrolysis.

3. Paste physico-chemical properties

3.1. Densification properties

The evolution of green density versus the number of strokes by the FSR equipment is shown in Figure 1 for the five pastes. Two samples per paste were densified, but as the curves for both samples are almost identical, only one has been represented for clarity reason.

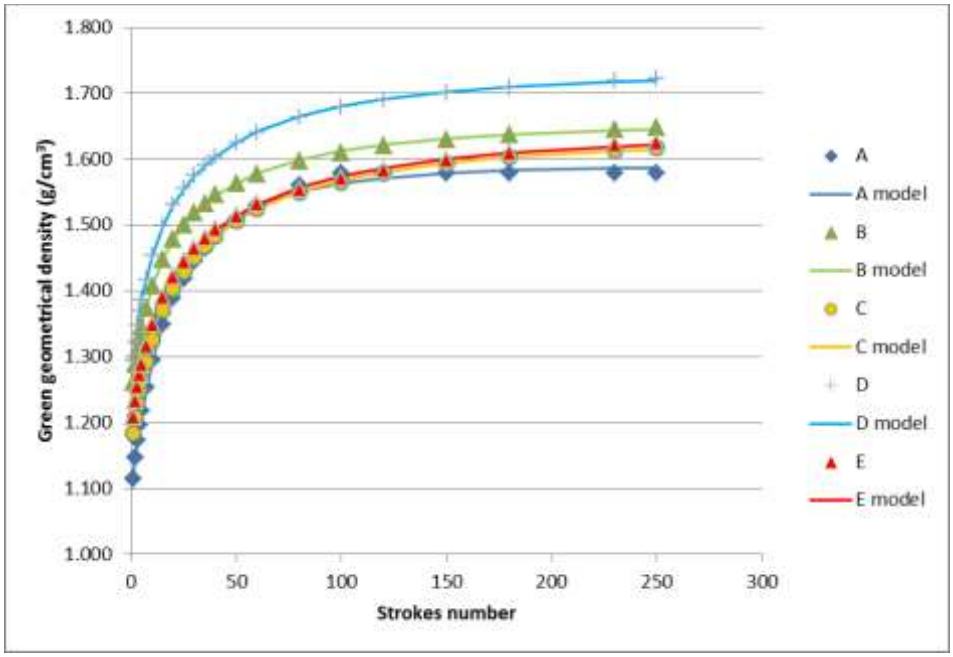

Figure 1. Green density curves versus number of strokes for the five pastes.

A higher density is achieved with paste D, but is similar for the other pastes above 1.600 g/cm^3 except for paste A, which has the lowest density. The curve for paste B has a different pattern, with higher densities than the other pastes even for a low number of strokes. These curves can be modeled and from the model, the rammability index N2 and the maximum green density can be determined. The average values calculated from the two curves for each paste are given in Table 5.

Table 5. Rammability index N2 and maximum density (ρ_{max}).

Type of paste	A	B	C	D	E
N2	63	97	123	104	138
ρ_{max} (g/cm^3)	1.591	1.654	1.632	1.742	1.646

Paste A has the lowest rammability index, and paste E the highest. Paste E may require more energy to become fully densified.

On the larger samples densified by a hand-rammer, the hydrostatic apparent density of pastes was measured at the green stage, again with a good reproducibility between two samples of the same paste. The average values of the two samples for each paste are given in Table 6 and show a good correlation with the maximum density determined with the FSR (Figure 2).

Table 6. Average hydrostatic apparent green density(HAD) for each paste (g/cm³).

Type of paste	A	B	C	D	E
HAD (g/cm³)	1.608	1.640	1.610	1.674	1.645

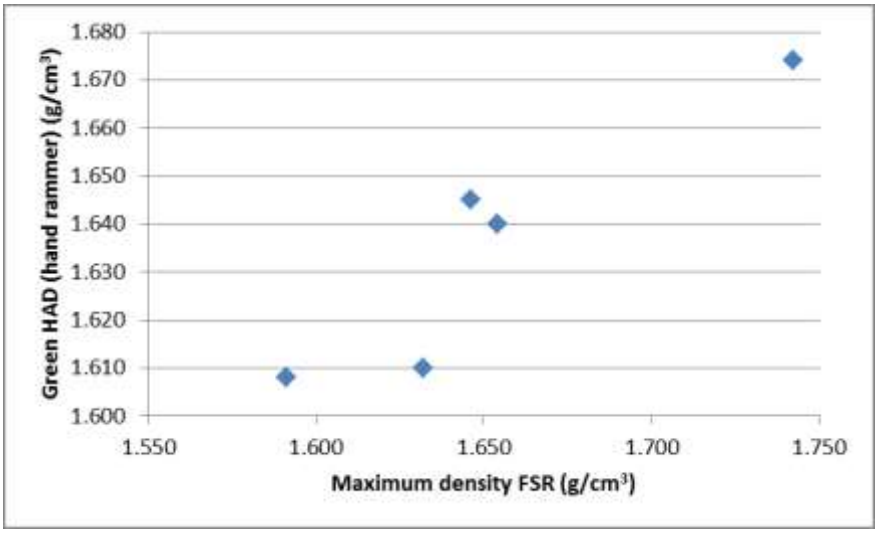

Figure 2. Relation between maximum density given by the FSR and the apparent green density given by the hand-rammer.

3.2. Properties after baking

The characteristics of each paste after baking at 1 000 °C are given in Table 7. As two samples were densified, the second one with a larger amount of paste to perform electrolysis tests, some measurements of density and volumetric expansion were performed on each individual sample, and both values are given in Table 7. The other characteristics have been measured on cores taken from the samples.

Table 7. Comparison of paste properties after baking.

Paste	Baked density	Weight loss (%)	Volume expansion (%)	Thermal conductivity (W/m.K)	Real density	Crushing strength (MPa)	Flexural strength (MPa)	Young's modulus (GPa)	Open porosity (%)	Total porosity (%)	Electrical resistivity (µΩm)	Ash content (%)	Oxidation (%)
A	1.450	9.7	0.2	5.0	1.857	12.7	2.1	3.6	19.1	20.8	92.0	6.6	6.6
A'	1.443	9.6	0.7										
B	1.431	12.2	0.6	5.0	1.825	17.4	3.3	7.3	18.8	20.6	70.4	3.3	4.5
B'	1.428	12.2	0.8										
C	1.468	8.8	-0.1	7.5	1.862	15.6	2.9	4.2	18.3	20.6	70.0	2.9	4.5
C'	1.464	9.0	0.1										
D	1.539	9.3	-1.2	12.1	1.976	19.9	4.1	4.9	19.0	21.6	47.7	4.6	9.9
D'	1.516	9.8	-0.5										
E	1.403	11.9	3.3	7.5	1.938	18.2	4.3	7.3	22.6	25.8	48.6	2.3	5.2
E'	1.381	12.6	4.1										

Density after baking shows values ranging from 1.38 to 1.40 g/cm³ (paste E) up to 1.52 to 1.54 (paste D). Generally speaking, the higher the baked density, the lower the volume expansion. Figure 3 illustrates this trend well. Paste D exhibits volume shrinkage during baking.

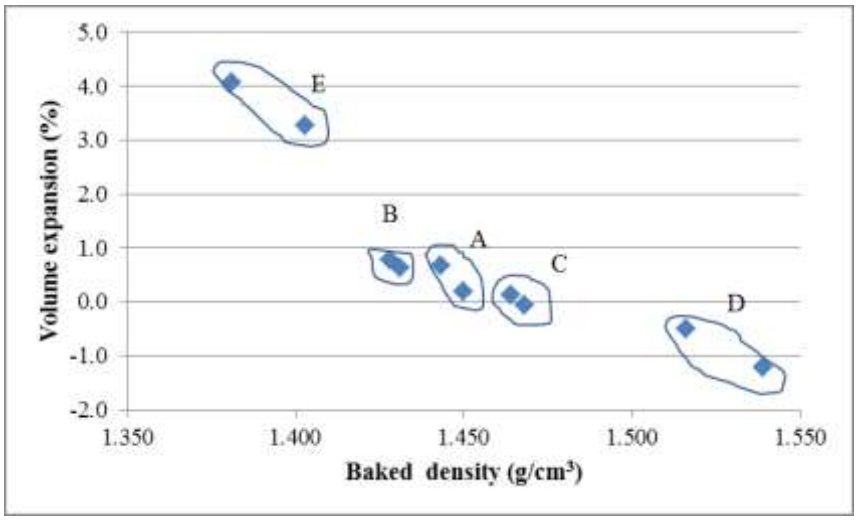

Figure 3. Relation between volume expansion and baked density.

The level of baked density depends on the paste formulation, binder level and binder nature. Pastes B and E, with a lower baked density that is also linked to a higher weight loss during baking, do not contain any PAH in their composition, and their binder nature affects the final baked density. Pastes A and C appear eco-friendly and probably have the same binder nature. Paste D seems to contain standard coal-tar pitch binder, and is on the high side in terms of baked density.

Regarding mechanical properties, the correlation between both crushing strength and flexural strength is also good (Figure 4). There is a good correlation with Young's modulus as well. Paste A presents the lowest mechanical properties, whereas pastes D and E are on a higher range.

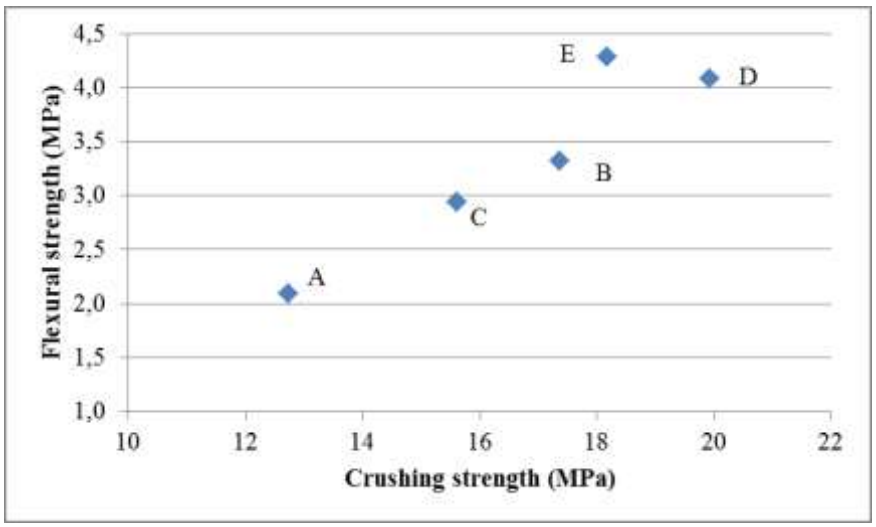

Figure 4. Relation between flexural strength and crushing strength.

The electrical resistivity values show three families of paste: pastes D and E with the lowest values are probably semi-graphitic pastes (which explains the high mechanical properties); pastes B and C present values typical of 100 % anthracitic paste; and paste A, with a very high electrical resistivity combined with the highest value of ash content, probably contains another type of raw material.

The conclusions are not as clear for the thermal conductivity values. The dependence of thermal conductivity on temperature has been determined with the Kohlrausch method [3], in parallel with the dependence of electrical resistivity on temperature and the values at 1 000 °C are given in Table 8. They confirm the lowest values of thermal conductivity for paste A. At 1 000 °C, all pastes present a

higher conductivity than at 30 °C, in a range between 12 and 16 W/m.K. The electrical resistivity values at 1 000 °C are lower than the values at room temperature.

Table 8. Thermal conductivity and electrical resistivity at 1 000 °C.

Type of paste	A	B	C	D	E
Thermal conductivity at 1 000 °C (W/m.K)	11.9	13.1	13.9	16.2	13.9
Electrical resistivity at 1 000 °C (μΩ.m)	67	52	48	36	37

The oxidation resistance of the five pastes varies from a weight loss of 4.5 % (pastes B, C, E) up to 9.9 % (paste D).

4. Emissions during baking

4.1. Follow-up test

Emission measurements in pots are very difficult and expensive. They require heavy pumps to be carried and changed regularly during the whole baking operation. Therefore a laboratory test has been developed at Carbone Savoie with the help of an external company, Explorair, which has strong expertise in VOC follow-up. Explorair has developed mobile equipment that can analyse the VOC up to C_8 on line and in situ, even on industrial sites. A method to follow-up not only VOC but also PAH, has been developed and was used to characterise the emissions during the baking of ramming pastes.

For VOC, the equipment consists of a μGC-MS (micro gas chromatography coupled to a mass spectrometer), with four columns of gas chromatography for VOC and permanent gases. A sample is taken every 4 minutes and treated in less than 1 minute with the help of a library of more than 250 000 species. All species can be detected and identified versus time. Taking into account the flow rate, the amount of each species expressed in mg per kg of paste sample can be calculated.

For PAH measurement, particles and gases are collected and adsorbed (on filters and tubes respectively). The tubes are injected after the test in a thermodesorber linked to gas chromatography and mass spectrometer (Fast TD-GCMS). The filters are chemically analysed with a solvent.

For the test developed for ramming pastes during their baking up to 1 000 °C, the tubes and filters are removed and replaced at each 100 °C interval, to follow the evolution of the amount of PAH or of heavy volatiles versus temperature. Light VOC and permanent gases are measured every 4 minutes. The baking rate chosen for the test is 180 °C/min, thus giving a total duration of 5.5 hours.

The ramming paste samples were those densified with the FSR equipment (which represents 180 g of paste). The samples are put in the dilatometry during baking equipment inside a specific reactor. The top of the reactor has been specifically designed to avoid condensation of the volatiles under the top, with an input of nitrogen (2 500 ml/mn) to push all gases emitted by the sample at the output of the reactor, where they are either condensed on the filter (for PAH particles), or collected by the tube (gaseous PAH or heavy VOC), or sent directly to the μGC-MS (light VOC + permanent gases). A picture of the equipment is given in Figure 5 and the detection limits are indicated in Table 9.

Figure 5. Equipment to follow-up PAH and VOC emissions during paste baking.

Table 9. Detection limits for VOC.

Molecules	Methods of measurement	Detection limit per molecule (ppm)
O_2, N_2	µGC/TCD	100
Methane, CO	µGC/TCD	40
H_2, CO_2, light VOC C_2 to C_3	µGC/TCD	5
Light VOC C_3 to C_9	µGC/TCD/MS	1

The concentration of each compound detected is calculated for each 4-minute sample and the whole emissions curve can then be represented versus time. Figure 6 presents an example of the curve obtained for paste C for two chemicals detected: ethylbenzene and benzene. Temperature is plotted versus time on the pink curve.

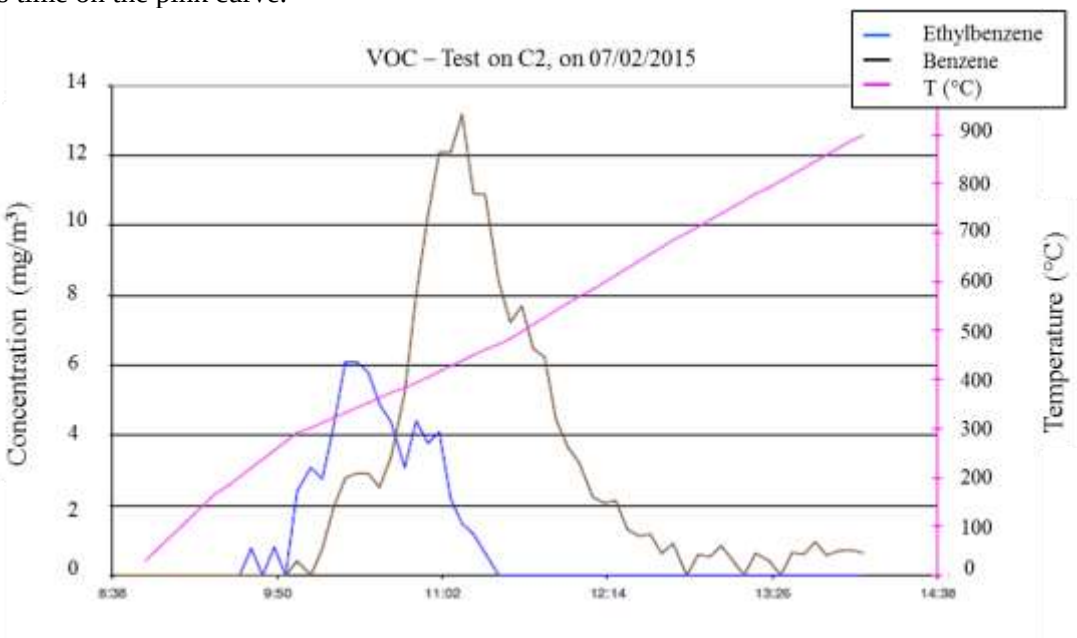

Figure 6. Example of a kinetic curve of ethylbenzene and benzene emissions in paste C.

It is not relevant to compare concentrations, but more important to calculate the weight released in mg and to divide it by the sample weight. This calculation takes into account the flowrate. The total amount of emissions could thus be compared in mg/kg between all pastes.

For paste A, which releases a high level of PAH during baking, a sample of 180 g is too big, and even when tubes and filters were changed each 100 °C, there were so many heavy compounds that the condensates blocked the pump that sent the gas to the analyser. It was decided to decrease the amount of paste to 50 to 70 g of paste. This amount was used also for pastes C and D, which initially presented a high level of PAH in their composition.

4.2. Comparison of the PAH emissions during paste baking

All tubes and filters taken every 100 °C were analysed and the amount of volatiles and particulates calculated. Figure 7 shows as an example of the gaseous PAH emissions versus temperature for paste C. Most PAH are emitted between 200 °C and 600 °C.

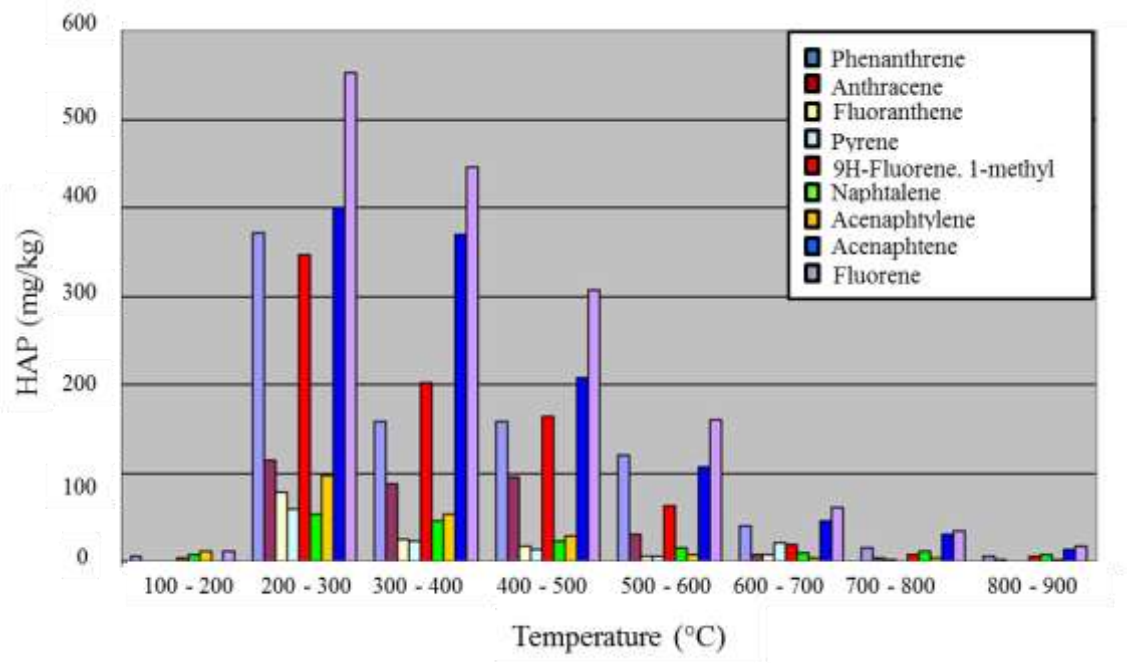

Figure 7. Emission of gaseous PAH versus temperature for paste C.

For high PAH releases, the top of the reactor becomes yellow from about 300 °C, then red around 500 °C, and above this between red and black. The results in Table 10 allow a comparison of the total PAH emitted, with a special focus on the 16 individual PAH (gas + particles). Individual PAH are designated by their shorten names (see Table 3). The ETF is calculated.

Even during baking, pastes B and E either do not release PAH, or only a small amount of light ones with no toxicological effect. Surprisingly paste A, which is EF, releases the largest amount of PAH during baking, and the ETF is almost at the level of the standard paste D.

Table 10. PAH and ETF comparison.

(mg/kg)	A	B	C	D	E
FA	507		284	553	
BbjFA					
BkFA	200		39	665	
BaP	158		50	302	
IP	37				
BghiP	136		11		
NA	680	50	174	1 548	59
AC	4 138	11	2 104	1 744	20
FL	2 114	15	2 546	338	33
PH	1 439	12	1 379	351	26
PY	452		233	501	
BaA	3			97	
CH	3			20	
ACY	297		306	404	
DiahA	84		20	17	
ANT	326		403	199	7
BbNT					
PAH sum	10 573	88	7 549	6 738	146
ETF	**251**	**0**	**82**	**323**	**0**
CO2	<LD	12 391	224	1 315	13 182
CH4	1 383	1 287	673	805	1 306
CO	679	5 823	818	1 609	5 868
H2	181	813		2 106	742
Permanent gas	**2 244**	**20 314**	**1 715**	**5 834**	**21 098**
Total VOC	**84**	**5 166**	**133**	**101**	**6 009**
BTEX	50	169	133	71	130

5. Performances in EGA DUBAL pots

5.1. Pot operating parameters

Samples were selected from the same potline, the same technology and design, the same cathode block and the same collector bars, with pot age differing by a maximum of ± 50 days.

- 4 samples from NeO² ramming paste,
- 4 samples from supplier A,
- 1 sample from supplier B.

In the data shown against pot age in Figures 8 to 11, there is a maximum time difference of 100 days since not all pots were started at the same time. This can be clearly seen in the amperage graph.

The data for the parameters in the figures show that there is no significant difference, beside the normal process variations, between pots with NeO^2 paste and pots with other pastes.

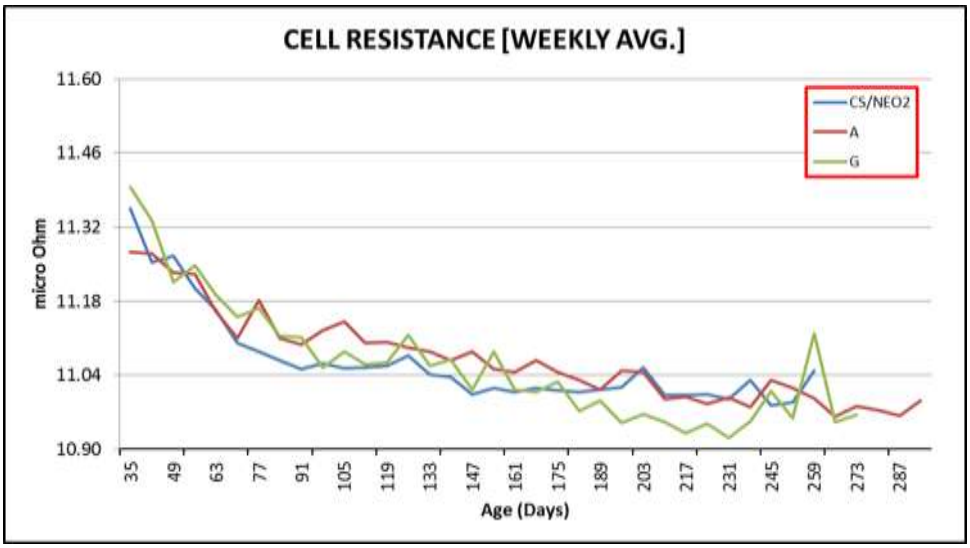

Figure 8. Cell resistance weekly average values for pots with different pastes.

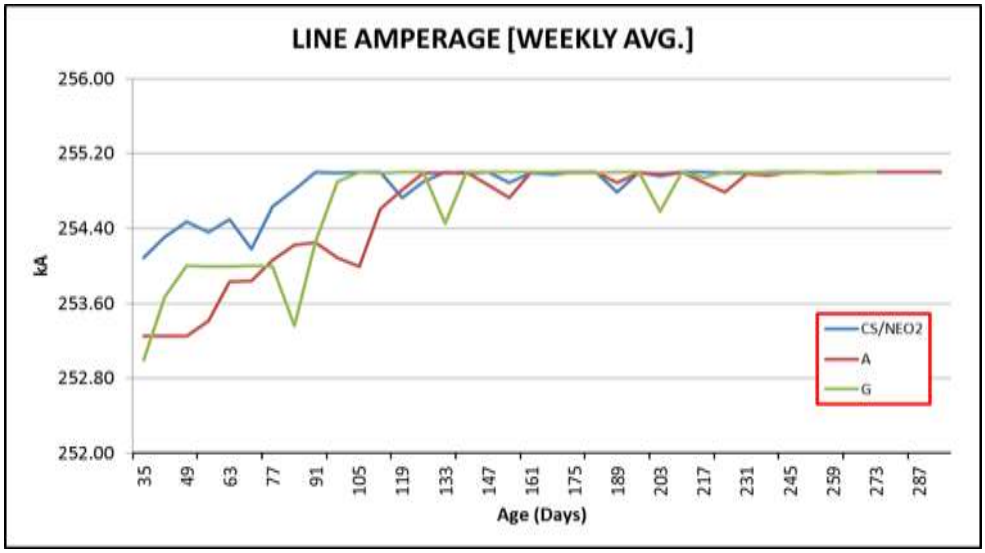

Figure 9. Line amperage average weekly values for pots with different pastes.

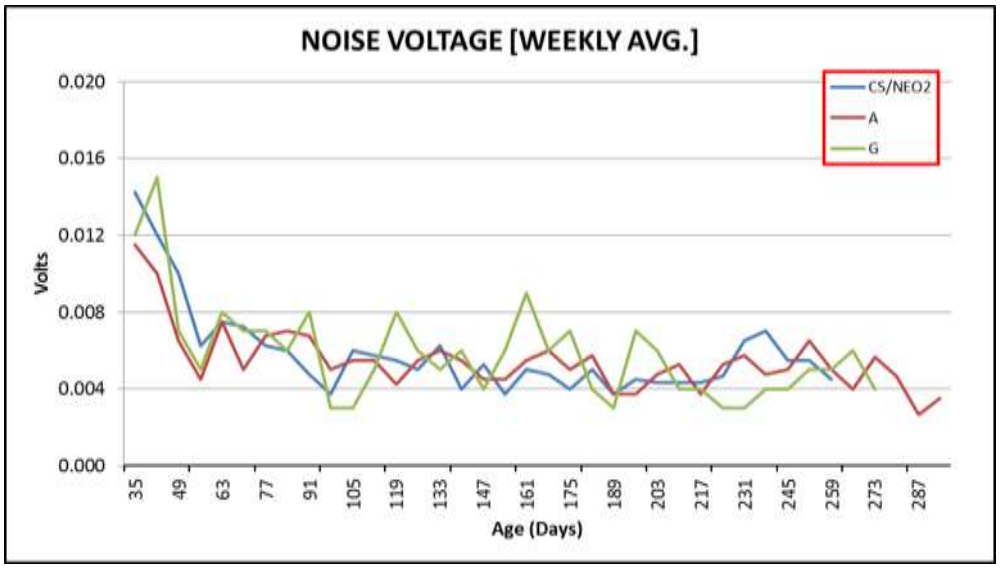

Figure 10. Noise voltage average weekly values for pots with different pastes.

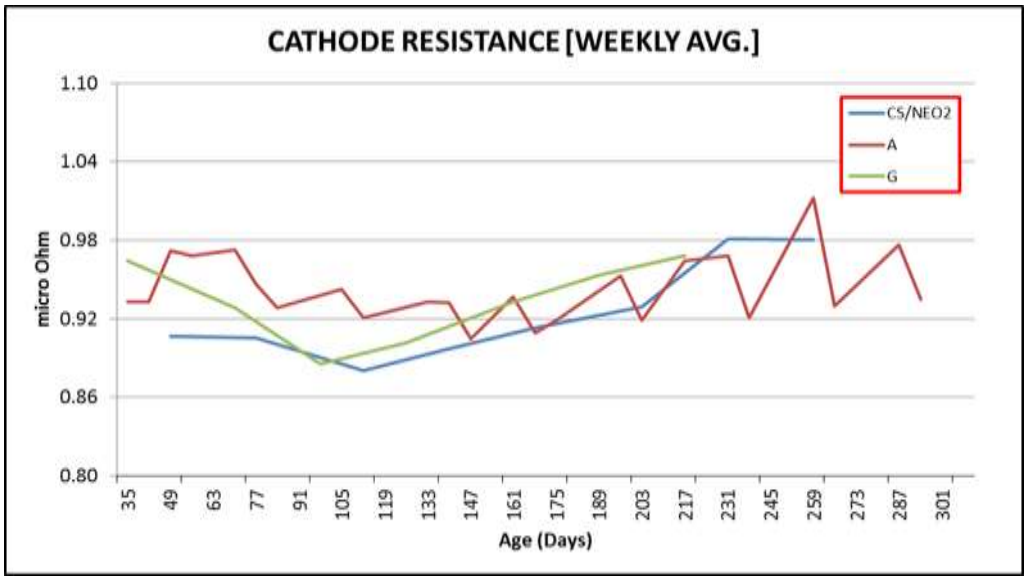

Figure 11. Cathode resistance average weekly values for pots with different pastes.

5.2. Pot age distribution

Trials of NeO^2 pastes started in DUBAL in 2011, involving two pots. The trial expanded in 2012 and 2013. After the material was approved in July 2013, larger quantities were procured. Figure 12 shows distribution of pot age of operating pots using NeO^2 and $CleO^2$ in DUBAL as of October 2015.

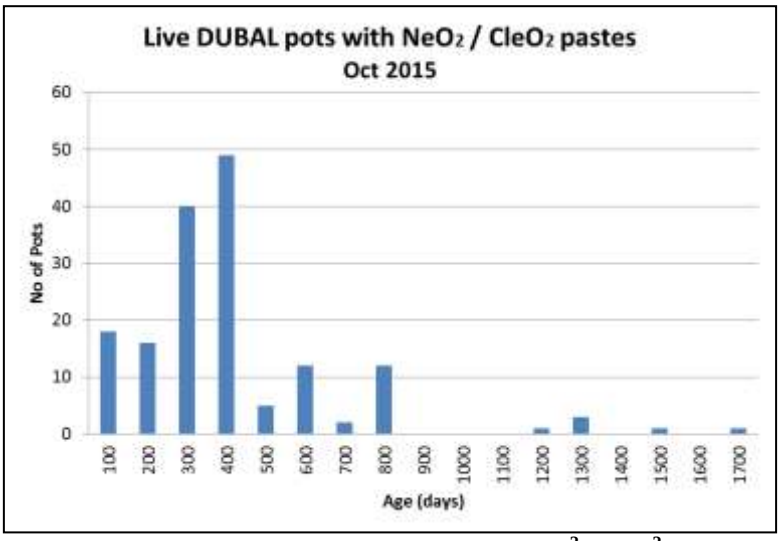

Figure 12. Pot age distribution for DUBAL pots with NeO^2/$CleO^2$ pastes, October 2015.

5.3. Cut-out pot cavity clean

Due to different expansion projects in D18 and DX Technology, there was an opportunity to inspect pots rammed with NeO^2 and $CleO^2$ pastes at ages 680 days and 369 days, respectively. As per Figures 13 and 14, no evidence of negative behavior regarding paste performance was observed so far, either in D18 pots with graphitic cathode blocks or in DX pots with graphitized cathode blocks.

Figure 13. Cleaned D18 pot cavity with NeO^2 paste at 680 days.

Figure 14. Cleaned DX pot cavity with $CleO^2$ paste at 369 days.

5.4. Preheat and start-up

Pot preheat was normal, following standard practices. Figure 15 shows the preheat temperature evolution during preheat. All pastes show normal preheat temperature. After the bath-up, there were no observations of peculiar behaviour during pot start-up and no leakage of bath or metal in pots with the tested ramming pastes. All parameters were similar to pots with regular approved supplier material.

The different pastes were used in EGA in different potlines. All pastes behave the same and the pots performance is good.

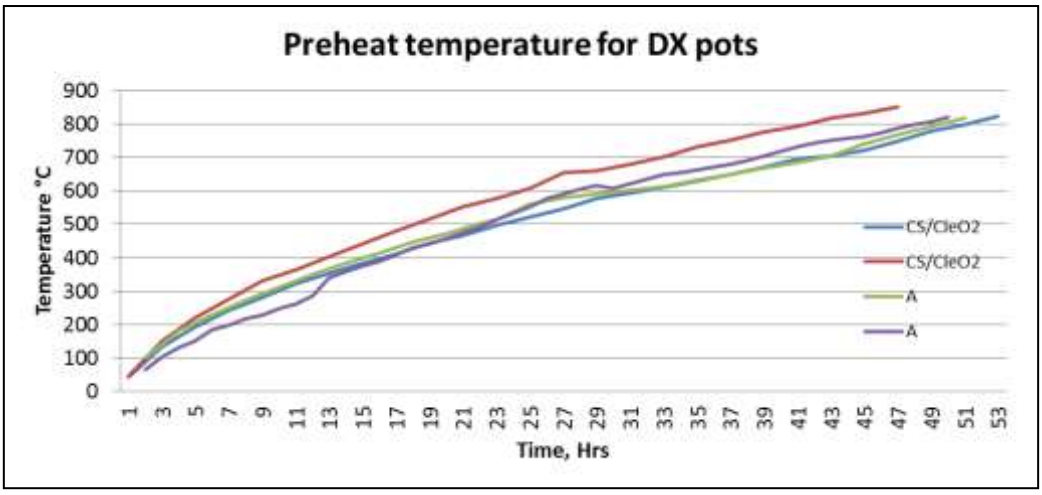

Figure 15. Preheat temperature for DX pots with different pastes.

6. Conclusions

Various ramming pastes, including eco-friendly (EF) and 100 % clean pastes, have been analysed. Their chemical and physical properties show some differences between pastes. A test to monitor the emissions during baking of the pastes has been developed and the results are presented. The performance of these new types of clean pastes in EGA pots is good and does not differ from other pastes.

7. References

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